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PHOTOGRAPHIC SCIENCE AND TECHNIQUE

A quarterly technical supplement to PSA Journal

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Formaldehyde as a Photographic Developer

GEORGE EHRENFRIED*

ABSTRACT

Although formaldehyde has often been used as a subsidiary component of developers, the fact that it can act as an independent developing agent is not widely known. Formaldehyde in strongly alkaline solutions acts as a developer of low potential and rather low selectivity. It develops chloride emulsions quite rapidly, but has little effect on bromide emulsions. Chloride ion acts as a very helpful restrainer for it, and bromide ion strongly inhibits its activity. Pictures of reasonably good quality have been made in developers consisting of: (a) paraformaldehyde, (b) sodium hydroxide or sodium sulfite, and (c) sodium chloride. The keeping and exhaustion characteristics of these developers are poor.

THE chemical formaldehyde (CH_2O) has a number of uses in photography. Its most common function is to harden the gelatin of films so they can survive long and severe processing procedures. Another well-known application is that of supplying alkali to developers by reaction with sodium sulfite. This reaction, which is used in developers for high-contrast graphic arts films, has been discussed by Willcock[1] and Yule[2]. A fact which is not widely known, however, is that formaldehyde itself has developing properties. Only one reference to such properties has come to the writer's attention, a statement in a book by Eduard Valenta[3] that it can develop a latent image in collodion-silver-bromide emulsions. Tennant-Woods[4] mentioned what he called development by formalin "in conjunction with hydroquinone", but examination of his formula shows that the hydroquinone was doing all the developing and the formalin was supplying the alkali. This paper will discuss some of the properties of developers which use formaldehyde as the only developing agent.

General Properties

Formaldehyde itself is a bad-smelling gas and in this form is not easily handled in photographic use. It exists, however, in two other more convenient forms. The first is formalin, a solution of formaldehyde in water with a concentration of about 400 grams per liter, containing also around 100 grams per liter of methyl alcohol. The second is paraformaldehyde (PFA), sometimes inaccurately called trioxymethylene, a dusty white powder consisting of about 95% formaldehyde and about 5% water combined together in large polymer molecules. PFA does not dissolve in water, but in alkaline solutions the polymer breaks down and the powder dissolves. In most of the experiments reported here PFA was used instead of formalin because of its better constancy of strength and freedom from impurities.

Two of the chemical properties of formaldehyde solutions are of interest. In the first place, like other substances such at hydrogen peroxide, it can act both as an oxidizer and a reducer. When it acts as an oxidizer, it is changed to methyl alcohol and when it acts as a reducer, it is changed to formic acid.

$$CH_2O + 2H^+ + 2e \rightarrow CH_3OH$$

$$CH_2O + H_2O \rightarrow HCOOH + 2H^+ + 2e$$

A form of this reducing reaction is what takes place when formaldehyde develops photographic emulsions. Like some other compounds of this type, formaldehyde can destroy itself by a combination of the oxidation and reduction reactions.

$$2\,CH_2O + H_2O \rightarrow CH_3OH + HCOOH$$

This "Cannizzaro Reaction" which takes place gradually in alkaline solution, is the chief process which sets a limit to the shelf life of a formaldehyde developer.

* Polaroid Corporation, Cambridge, Massachusetts. Presented at the PSA National Convention in Detroit, Michigan 13 October, 1951. Received 8 October 1951.

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The second interesting chemical property of formaldehyde is its ability to combine with sodium bisulfite,

$$CH_2O + NaHSO_3 \rightleftharpoons CH_2O \cdot NaHSO_3$$

This reaction goes to completion in neutral solutions, but in alkaline solutions it is incomplete and reaches equilibrium. In the presence of formaldehyde, sodium sulfite is hydrolyzed to sodium hydroxide and sodium bisulfite, which proceeds to combine as above.

$$CH_2O + Na_2SO_3 + H_2O \rightleftharpoons CH_2O \cdot NaHSO_3 + NaOH$$

This is the reaction by means of which formaldehyde and sulfite furnish alkali for graphic arts developers, as mentioned in the first paragraph.

The power of formaldehyde and other aldehydes to reduce some silver salts to silver metal has long been used in analytic chemistry in the "silver mirror" test for the presence of aldehydes. A photographic application of formaldehyde's reducing power is that of Blake-Smith and Garle[5] who suggested its use as a redeveloper in the Monckhoven intensifying process. Formaldehyde's reducing strength is much lower than that of the developing agents in common use. While it reduces soluble and slightly soluble silver compounds, it does not reduce at a useful rate those silver compounds or complex ions having oxidation potentials (relative to hydrogen) more positive than about — 0.15 volts. In other words, silver compounds or complexes of which the pK_2 is higher than about 11 are not reduced readily. (pK_2 = negative log K/n where K = solubility product or dissociation constant and n = number of silver ions resulting when a molecule of solid or an ion of complex dissociates.) In this respect formaldehyde is similar to some other compounds, such as sodium quinone sulphonate,[6] which are reported as being developers for silver chloride emulsions but not for silver bromide.

Formaldehyde in water solution exists mostly in the hydrated form called methylene glycol, which can ionize as a very weak acid.

$$H_2C(OH)_2 \rightleftharpoons H_2COOH^- + H^+$$

Since the dissociation constant of this acid is 1.62×10^{-13} at room temperature,[7] it does not ionize appreciably except in alkaline solutions with pH above about 11. Since, as with most developers, it is the ion which is the active reducer, formaldehyde solutions do not develop unless made strongly alkaline. The overall reaction of development thus takes the following form:

$$2\ AgCl + CH_2O + 3\ NaOH \rightarrow 2\ Ag + NaCOOH + 2\ NaCl + 2\ H_2O$$

Types of Photographic Materials

Formaldehyde developers give silver images when used with silver chloride photographic materials. Contact printing papers made by several manufacturers and of several emulsion types (blue-black, neutral, and warm-tone portrait types) and of all the contrast grades have shown images of varying quality. Best results have been obtained with the No. 2 grade of the blue-black or neutral types of contact paper, and this has been used for most of the experimental work. The various contrast grades of the same type of paper do not fit into a smoothly-changing series of steps from low to high contrast, but instead large jumps in speed, contrast, and fog are found between adjacent paper grades. The paper speed obtained with formaldehyde developers is much lower than with Metol-hydroquinone, about one tenth or less of normal speed, A conspicuous feature of these developers is the remarkably long exposure scale they give. It is hard to develop a negative, even if made on fairly contrasty camera film, so much that it will give a contrasty print. It is probable that the chief use which may be made of formaldehyde developers in practice would be as a means of getting prints of reasonable quality from negatives so contrasty that no ordinary paper-developer combination will cover their density scale. Figure 1 shows a comparison between the characteristic curves obtained with formaldehyde and with normal paper developer on No. 2 contact paper.

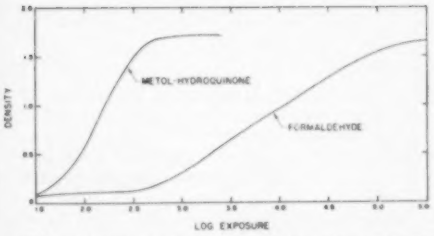

Figure 1. Characteristic curve of Azo F-2 developed for one minute in 40 PFA + 20 NaOH + 6 NaCl, compared with curve for D-72 type Metol-hydroquinone development.

Other materials besides contact papers give images in formaldehyde. For instance, rather weak images are obtained with the high-contrast graphic arts "-lith" films, and process films give very faint images. Fairly good results are often obtained with experimental silver chloride films made by rehalogenizing developed silver in permanganate-chloride-sulfuric acid bleaches. Camera negative films usually darken very slowly in formaldehyde developers, so that after long treatment in a very active developer there is density somewhere between zero and 0.4 (depending on the type of film) with no image.

The System Formaldehyde-Alkali

The simplest developer system for study consists of paraformaldehyde and sodium hydroxide in water. This is a poor developer but has some interesting properties. The sodium hydroxide concentration has the expected effect; increasing the NaOH increases the developer activity. In the range from 5 to 40 grams per liter NaOH, the development rate increases about as the 1.8th power of the NaOH concentration. The PFA concentration has a much different effect. When it is very low, the solution does not develop but fogs non-selectively. As the concentration increases, the selectivity increases, leveling off at about 40 grams per liter. From here on up, the selectivity remains nearly constant, but the developing rate slows down considerably. This effect is shown in Figure 2, which applies to a developer containing a constant 10 grams per liter of NaOH and varying concentration of PFA. The rate of develop-

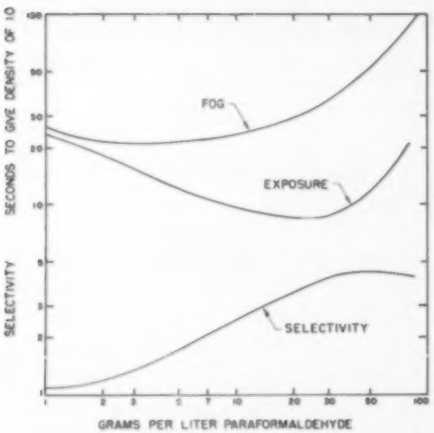

Figure 2. Effect of paraformaldehyde concentration on the development rate for exposed areas and fog, showing the change from fogging action to developing action with increasing concentration. Sodium hydroxide concentration is 10 grams per liter.

ment for exposed areas and fog is indicated by the time required to reach a density of 1.0 in each case, and the selectivity is taken as the ratio between the two times.* No explanation has been found for the change from fogging action to developing action as the PFA concentration is increased, or of the decrease in developer activity when it is increased still more.

Other reasonably strong alkalis, such as sodium carbonate and trisodium phosphate, can ionize formaldehyde enough to make it develop, but the development rate is much slower than with sodium hydroxide.

The System Formaldehyde—Sodium Sulfite

Because of the previously mentioned sodium bisulfite addition reaction, it is possible to make developers consisting of formaldehyde and sodium sulfite. The properties of these developers are similar to those made with sodium hydroxide rather than those made with the weaker alkalis. Comparison of the developing rates of sodium sulfite and sodium hydroxide developers shows that, in the alkalinity range that exists in these developers, the bisulfite addition reaction comes to equilibrium between a quarter and half way to completion. For instance, 63 grams per liter of sulfite (0.50 moles) gives a developer with activity equal to that given by 9 grams per liter of sodium hydroxide (0.225 moles). Since the equilibrium position of the addition reaction depends on the alkalinity of the solution, going more nearly to completion in less alkaline developers, the sulfite developers are buffered as compared with the sodium hydroxide developers. Adding a given amount of strong acid (sulfuric) or strong alkali to a sodium sulfite developer makes only about half as much change in its photographic activity as the same addition to the corresponding sodium hydroxide developer.

Restrainers

Anions which combine with silver to make compounds or complexes of higher insolubility or stability than silver chloride decrease the activity of formaldehyde developers. In general, the effect of a small amount of such substance is to slown down the development rate and paper speed and decrease the selectivity. An intermediate amount gives a brown image which, with emulsions on paper, is often very grainy. A large amount suppresses development completely. In some cases development goes part way and then stops, the precipitation or complex-forming reaction having used up the silver chloride. Bromide, iodide, thiosulfate, and thiocyanate are anions which were found to have these effects.

Chloride ion is a special case. It is the only material so far found which increases the selectivity of formaldehyde developers. The chloride, by common-ion effect, reduces the solubility of the silver chloride and therefore restrains the development reaction without, however, combining with the silver ion to form unreducible compounds. Figure 3 shows how sodium chloride slows down development both for fog and for exposed grains and how it increases the selectivity over three times by having more effect on the fog. Aside from its anti-fogging action, the general slowing-down effect of sodium chloride helps by giving development times of from 1 to 5 minutes instead of the uncontrollable 5 to 15 seconds of unsalted developers. Typical formulas that have been used for making pictures contain 40 grams per liter of paraformaldehyde, 5 to 20 grams per liter of sodium hydroxide, and 3 to 12 grams per liter of sodium chloride. Developers with high chloride concentrations give warm toned images. It is evident that there is a fairly good analogy between the behavior of chloride ion in a formaldehyde developer acting on silver chloride emulsions and of bromide ion in a Metol-hydroquinone developer acting on silver bromide emulsions.

Various other addenda have been tried in formaldehyde developers. Sulfate, citrate, tartrate, oxalate, and ferrocyanide, used in moderate amounts, had little or no effect on the appearance of the sample. Ammonia made the tone a little bluer and in large amounts increased the fog. Methyl alcohol and benzotriazole both decreased the activity of the developer without improving the selectivity. Sodium formate, unexpectedly in view of the observations of James[8] on the effect of developer oxidation products, increased the activity of the developer—the only chemical found to do this.

Keeping Properties

Strongly alkaline formaldehyde solutions are rather unstable, losing strength by aerial oxidation, the Cannizzaro reaction, and probably other reactions. These changes are fast enough so that quantitative measurements should not be done with developers more than about one hour old, although pictures can be made with older solutions by increasing the development time. Photographic tests of

* The material tested was Kodak Azo F-2, the exposure was 60 seconds at 5,600 meter candles from a No. 1 Photoflood, and the developing temperature was 68°F. The original data showed that for densities different from 1.0 the image and fog curves would have essentially the same shape and relative positions although they would be higher or lower on the time axis.

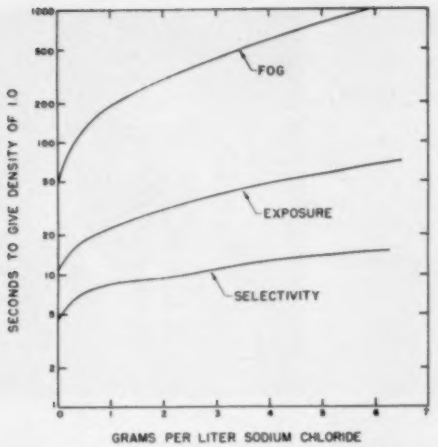

Figure 3. Restraining effect of sodium chloride on developer containing 40 g.p.l. of PFA and 10 g.p.l. of NaOH.

reaction rate were made with 40-20-6* developer. Samples were processed in solutions that had been kept unused in closed containers for various lengths of time, and the results compared with those obtained in a series of solutions which were made to have the compositions that the developer would have at various stages of progress of the Cannizzaro reaction. The resulting curve of reaction as a function of time looked about like a first-order reaction curve with a half-completion time of 30 hours.

The Cannizzaro reaction by itself would cause the loss of two molecules of formaldehyde for each molecule of alkali, while aerial oxidation alone would give a one-to-one loss ratio. Analytical tests, in which the formaldehyde concentration was measured by the sodium sulfite method described by Walker,[9] have shown loss ratios near two to one, supporting the assumption that the Cannizzaro reaction accounts for most of the loss. The photographic effect of a small loss is quite large. This suggests that inhibiting reaction products may have been formed, but it has been found that old solutions that have been replenished to initial analyzed strength behave photographically about like fresh solutions.

Exhaustion Properties

The apparent exhaustion of a formaldehyde developer, as shown by its photographic behavior, is very rapid. When a series of 5 x 7 sheets of contact paper are developed in 200 cc of 40-10-12 formula, each sheet loses about 0.2 logarithmic units of speed as compared with the previous sheet. Since the loss in formaldehyde and alkali after exhaustion, as determined by analysis, is very small, the rapid change in photographic properties must be caused by the accumulation in the solution of halides and perhaps other inhibiting chemicals which are freed from the emulsion, partly by washing out and partly as a result of the reduction of the silver. The rate of exhaustion of a sodium sulfite developer (40 g/1 PFA + 63 g/1 Na_2SO_3 + 6 g/1 NaCl) has been found to be the same as the corresponding sodium hydroxide developer (40-9-6).

* The first number represents the concentration, in grams per liter, of paraformaldehyde, the second number that of sodium hydroxide, and the third number that of sodium chloride.

Use of Formaldehyde with Hydroquinone

Tests were made to see whether formaldehye and hydroquinone showed any "superadditivity" when used together. Two developers containing 30 grams per liter of sodium carbonate as the alkali and with hydroquinone and formaldehyde as the reducers were made up. The concentrations were adjusted so that both developers gave weak images in four minutes, then the developers were mixed and more samples developed. The results did not show any evidence of superadditivity.

Conclusion

The foregoing description is not intended to intimate that formaldehyde is a good developing agent. As before mentioned, it is probable that the only case where its use in practical photography would be justified is where a contact print is to be made from an otherwise unprintable contrasty negative. Its chief interest lies in its possible use as a new tool for the study of the physics and chemistry of development, based on the fact that it is a simple compound, engaging here in comparatively simple reactions, and that its properties are in many ways very different from those of developers which have already been studied.

The writer desires to express his gratitude to the Polaroid Corporation for permission to undertake this investigation, to Miss Barbara Higgins and Miss Rhoda McCord for carrying out a large part of the experimental work, and to Lloyd Varden for helping with his knowledge of photographic history and literature.

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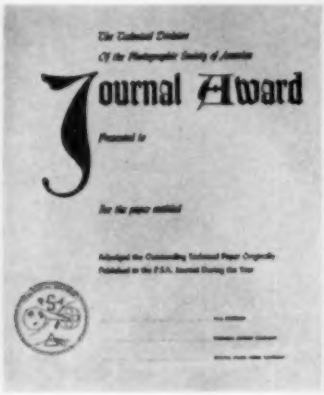
EDWARD B. NOEL, FPSA



PAUL B. DAVIS

TECHNICAL AND SCIENTIFIC PAPER AWARD FOR 1950 GOES TO E. B. NOEL AND P. B. DAVIS OF GENERAL ELECTRIC CO.

H. Clyde Carlton, APSA*

JUDGED the outstanding technical and scientific paper published by the PSA during 1950 *A New Low-Voltage Low-Power Flashtube of High Efficiency* by E. B. Noel and P. B. Davis has been given the Technical Division "Journal Award". The award was announced at the PSA Convention banquet in Detroit on October 13, 1951 and a scroll has been presented to the authors.

The Noel and Davis paper was published in the first issue of PHOTOGRAPHIC SCIENCE AND TECHNIQUE which appeared in January 1950 as Section B of the PSA Journal Volume 16, Number 1. The paper deals with the design and operating characteristics of the General Electric FT-110 Flashtube. By producing 75% more light than older Flashtubes when operated at 100 watt-seconds and at 1000 volts, this new photographic light source makes possible light-weight, extremely portable, as well as semi-portable, multiple flash equipment.

The authors are employed in the Lamp Development Laboratory of the General Electric Company Lamp Division at Nela Park, East Cleveland 12, Ohio. Mr. Edward Bernard Noel, FPSA, is a professional Electrical Engineer in charge of mercury lamp and flash tube development at Nela Park. He was born in St. Louis, Missouri in 1907, attended public school there and later received his B.S., M.S., and E.E. from the University of Illinois. He is a member of six collegiate honor societies, the Illuminating Engineering Society and the American Institute of Electrical Engineers. Mr. Noel operates amateur short-wave radio station W8GRY in Cleveland as a hobby and is also interested in high fidelity music reproduction. As a pictorial photographer he has exhibited widely in photographic salons.

Mr. Paul Bramley Davis is also a member of the Photographic Society of America and, like Mr. Noel, is active in the Cleveland Section of the Technical Division. Mr. Davis was born in 1906 at Mayfield Heights, Ohio and attended the public schools in East Palestine, Ohio. He studied for two years at Case Institute of Technology and had considerable experience in the radio field before joining the General Electric organization in 1930. His hobbies are photography and electronics, which he manages to dovetail with his work as an assistant development engineer concerned with flashtubes and mercury discharge lamps.

Award Committee Reviews all Papers

All the technical and scientific papers published by the Society during 1950 were reviewed by the Award Committee who found a very high level of quality in general. Selection of a single outstanding paper was, therefore, a difficult matter. The final choice of the Committee was unanimously approved by the members who represent not only the Technical Division but are broadly representative of the Society as a whole. Assisting the Chairman in this endeavour were the following judges of technical and scientific writing in the field of photography:

* Eastman Kodak Company, Rochester, New York. Received 4 January 1952. (Dr. Carlton is Chairman of the "Journal Award" committee of the PSA Technical Division.)

Herman H. Duerr, FPSA, Ansco Division, Binghamton, New York; from the Technical Division.

Frank E. Fenner, FPSA, Popular Photography, New York City; from the Motion Picture Division.

Glenn E. Matthews, FPSA, Kodak Research Laboratories, Rochester, New York; from the Technical Division.

George Allen Young, APSA, Camera Craft Publishing Company, San Francisco, California; from the Color Division.

Three additional papers, that also appeared in PHOTOGRAPHIC SCIENCE AND TECHNIQUE during 1950, were awarded Honorable Mention.

Harold E. Edgerton, FPSA, of the Massachusetts Institute of Technology, received Honorable Mention for his paper "Light Meter Uses with Electronic Flash" that was published in the January issue.

C. A. Morrison and H. O. Hoadley of the Kodak Research Laboratories received Honorable Mention for their paper on photographic instrumentation "A Spectrosensitometer" that appeared in the August 1950 issue.

H. D. Russell, E. C. Yackel, and J. S. Bruce of the Kodak Research Laboratories received an Honorable Mention for their paper "Stabilization Processing of Films and Papers". This paper also appeared in the August 1950 issue.

The Award Committee feels that annual recognition of the outstanding technical and scientific paper published by the Society is having an encouraging and stimulating effect on the technical literature in America. Since John I. Crabtree of the Kodak Research Laboratories was given the first Award for his 1949 paper titled *Rapid Processing of Films and Papers*, both the quantity and the quality of technical papers published by PSA authors have grown.

The scroll that accompanies the annual award for the outstanding technical and scientific paper is shown in the illustration. Thanks are extended to Albert Eyman of the Kodak Park Printing Division for the design. Thanks also are extended to the members of the Award Committee for their valuable assistance in making the 1950 selections.

REGULATIONS FOR THE TECHNICAL AND SCIENTIFIC PAPER AWARD

The PSA Technical Division "Journal Award" Committee shall consist of five members in good standing. This committee shall be appointed by the Chairman of the PSA Technical Division and confirmed by the Executive Committee of the Division.

The PSA Technical Division "Journal Award" shall be made on the basis of the following qualifications:

1. The paper shall have been published originally in the PSA JOURNAL, its Sections or Supplements, during the preceding calendar year.
2. The paper must deal with some scientific or technical aspect of the field of photography.
3. In judging the merits of the paper, three qualities shall be considered as follows:
   a. Technical merit and importance of material 45%
   b. Originality and breadth of interest 35%
   c. Excellence of presentation of the material 20%

A majority vote of the entire Committee shall be required for the election of the Award. Absent members may vote in writing.

The report of the Committee shall be presented to the Executive Committee of the Technical Division in the late summer meeting for ratification. At the national meeting of the PSA in the fall, a suitably embellished certificate shall be presented to the author or to each of the authors of the most outstanding paper.

Other papers may be cited for Honorable Mention at the option of the committee, but in any case should not exceed three in number.

These regulations, a list of all Journal Award recipients, the year of each Award, and the title of the papers shall be published at least annually in the PSA JOURNAL. In addition, the list of papers selected for Honorable Mention shall be published in the PSA JOURNAL during the year current with the Award.

Measuring the Image Tone of Photographic Paper*

Walter H. Carnahan

SUMMARY

A numerical method for expressing the image tone of photographic papers is described. Spectrophotometric measurements of reflectance at three wavelengths expressed in percent define the color of the image. Image tone is most noticeable at medium densities which give data indicative of the tone of the whole range of densities.

ALMOST ALL the factors associated with quality evaluations of photographic prints can be reduced to numerical terms. Contrast, speed, gloss and other physical characteristics have been put on an objective basis. The volume of use of such criteria indicates that wide acceptance has been given to sensitometric and physical testing. One of the last factors of photographic quality to be reduced to numerical terms is image tone. The Paper Service Division of the Eastman Kodak Company has been using since 1946 the system described in this report for numerical expression for image tone.

The advantages of numerical measurement for production control and for chemical experimentation are obvious. The goal that was set in deriving the present system was to provide a fast but accurate method which could be used by testing personnel for measurement of image tone on large numbers of samples. One important factor con-

* Paper Service Division, Eastman Kodak Company, Rochester, New York. Presented 13 October, 1951 at the PSA national Convention in Detroit, Michigan. Received 23 November 1951.

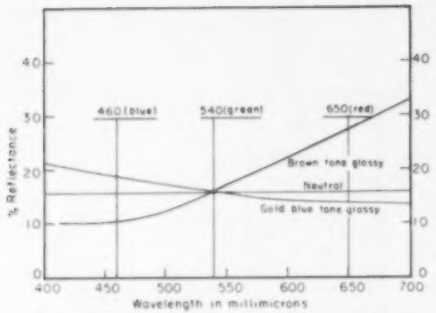


Fig. 1. Spectrophotometric curves of several paper samples of different image tone.

nected with image tone is that the image tone of photographic papers covers a limited range of colors. Tones of photographic papers are almost always desaturated colors. This limits the range of colors which need to be considered. On the other hand the eye is sensitive to extremely small variations in spectral reflectance. Instruments of very high precision are required to measure reproducibly the small differences in color which the eye is capable of detecting. Reflectance differences of 0.2% have been found to be quite significant.

The image tone of most photographic prints varies with the density level. Extreme highlights in a print obviously have the color of the paper stock and are independent of the silver emulsion. Likewise the color of the deepest shadows is controlled as much by the surface texture of the paper as by the silver deposit on it. At medium densities, differences in image tone are most recognizable. For production control purposes a system which yields different numbers for image tone at various density levels of the print would be too complicated. What is needed is a system which will give a description of the color or tone as a whole. The image tone of the paper should be identified by a single number which would describe the tone as a whole, independent of density level.

The science of color measurement has evolved over many years and it would seem that some method already in existence could be adapted for the measurement of image tone. This has not proven to be the case. There are an almost infinite number of colors in nature. The colors formed in photographic papers represent an extremely small portion of these. For this reason, methods which are satisfactory for expressing all the colors in nature are much too inclusive or complicated for image tone measurement of photographic papers.

The instrument best adapted for precise measurement of color is the spectrophotometer. A spectrophotometer permits the determination of a curve of percent reflectance as a function of wavelength. This curve is a fundamental and complete description of the color reflecting properties of samples. It is independent of light source. Figure 1 shows spectrophotometric curves of several paper samples of different image tone, all of which were selected to be of approximately the same density level. Curves of this type make it evident that warm tone papers have higher reflectance of red and relatively low reflectance of blue light. For blue-toned papers the reverse is true. Blue-toned papers have high reflectance of blue light and relatively low reflectance of red light. Similar curves have been determined for many samples at a wide variety of density levels.

Method of Measurement

In the interest of speed and ease of operation, it has been found necessary to adopt several approximations in establishing the image tone measurement system described. One of these depends upon the fact that the spectrophotometric curves of image tone samples are smooth. They do not show sudden changes of reflectance with small changes in wavelength. Because of this fact, reflectance values at three selected wavelengths can be taken as indicative of the full spectrophotometric curve. Dye-toned samples, on the other hand, exhibit spectrophotometric curves which are not smooth and for this reason the image tone measurement system cannot be employed with dye-toned samples. Three wavelengths were arbitrarily selected at 460, 540 and 650 millimicrons as representative of the blue, green and red reflectance of the sample. The basis of this method for measurement of image tone is to use the reflectances at these three wavelengths as a numerical expression of tone.

Variations of tone as a function of density level can be shown by determining the percent reflectance at various levels of density. Figure 2 shows the result of this sort

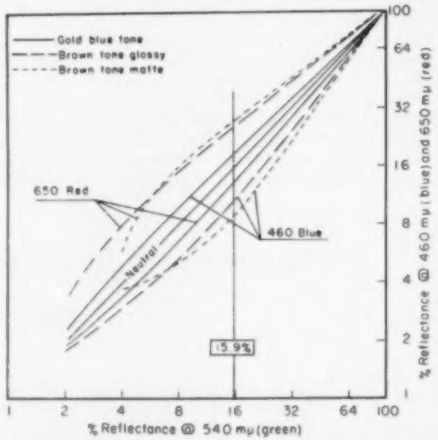


Fig. 2. Variations in blue and red reflectance plotted as a function of green reflectance of samples illustrate the variation of tone with density level.

of analysis. The reflectance at wavelength 540 $m\mu$ in the green is taken as indicative of the density level. In Figure 2 the reflectance at wavelengths 460 and 650 $m\mu$ is plotted as a function of the reflectance at wavelength 540$m\mu$. In Figure 2, percent reflectance is calculated relative to a fixed out sample of the paper stock. For this reason, the apparent reflectances approach 100 percent. Highlight areas are represented at the upper right hand corner of the figure.

Shadow densities are represented at the lower left hand corner. Separation between the red and blue reflectance is related to the noticeability of tone. Figure 2 shows that this separation is greatest for medium densities. Higher and lower densities show less separation between blue and red reflectance. Prints on matte surface papers, which exhibit a low maximum density, have their maximum separation in Figure 2 at a lower value of density (higher value of reflectance) than do glossy samples which are capable of higher maximum densities. In practice image tone measurements are made at a fixed density for all samples in the interest of simplification. For this reason, the image tone measurement is not necessarily at the most noticeably different density level for all surfaces. A density of 0.8 which is the equivalent of a reflectance of 15.9% was selected. If only glossy samples were to be read, it would be advantageous to use a somewhat higher density.

Measurement for calculation of image tone in these laboratories is done by means of a General Electric recording spectrophotometer modified by the addition of auxiliary lenses to read an area approximately ¼ inch in diameter. Readings are generally made from a continuously modulated sensitometric wedge strip rather than from a step tablet. Using such a strip an area having exactly 15.9% reflectance at wavelength 540 millimicrons can be found. It is also possible to make readings from areas of prints or from step-tablets which do not have precisely the required density. In such cases an interpolation must be made using charts of the type shown in Figure 2 to convert from the actual density to the characteristics of an area of the same paper which would have 15.9% reflectance at 540mμ. In actual operation the wavelength dial of the spectrophotometer is set for 540 millimicrons. The continuously wedged sample is then inserted in the reading position and moved along its length until an indication of 15.9% is obtained. At this position the sample is clamped stationary and the wavelength dial is turned successively to 460 and 650 millimicrons. Readings of an auxiliary Veeder counter are made at these two wavelength positions showing the percent reflectance. These three numbers constitute the measurement of image tone.

Graphical Representation

For some purposes, the three values of reflectance at chosen wavelengths are all that are required. For other purposes, it is desirable to plot the image tone as a point on a graph. Figure 3 shows how the image tone of a given sample is plotted as the vector sum of reflectances of the three wavelengths. The three reflectance values in Figure 3 are plotted 120° apart in the three directions as shown. A perfectly neutral sample would have identical reflectance at the three wavelengths and would plot at the origin (dashed lines). In practice, the reflectance value at wavelength 540 is always maintained constant and equal to 15.9% by selection of a suitable area of the sample or by interpolation from graphs like Figure 2. Therefore it is only necessary to plot the other two values.

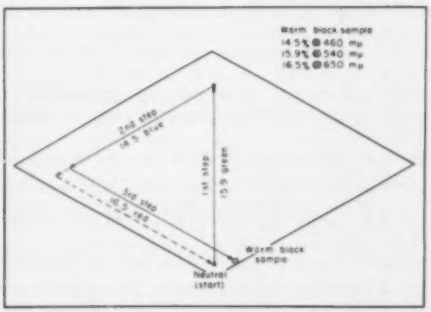


Fig. 3. The basic steps in plotting image tone rest upon the supposition that tone is the resultant of three vectors.

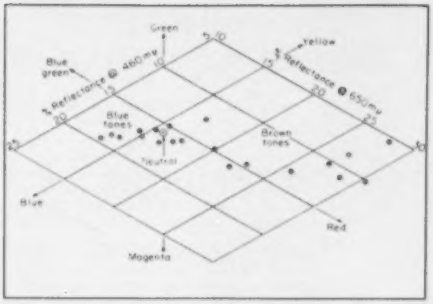


Fig. 4. Image tone plot of various prints showing the general arrangement in a horizontal array from cold blue tones to warm brown tones.

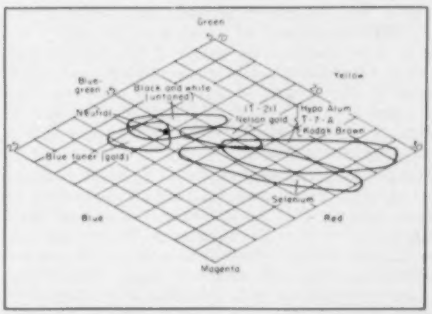


Fig. 5. Range of tones produced by chemical toners on a variety of paper types.

Figure 4 shows the result of plotting the image tone of a variety of paper samples. It is evident that most of these samples arrange themselves in a roughly horizontal line. This line is the representation of the general warm to cold variation in paper tones. The fact that certain samples are different from each other in directions at right angles to this line is an illustration that samples vary in other ways than just warmness or coldness. For this reason, a one number description of image tone is not possible.

Figure 5 shows the range of tones which have been recorded for samples treated in various toners as well as untoned samples. Different types of paper developed in normal developers cover a range of image tone near the

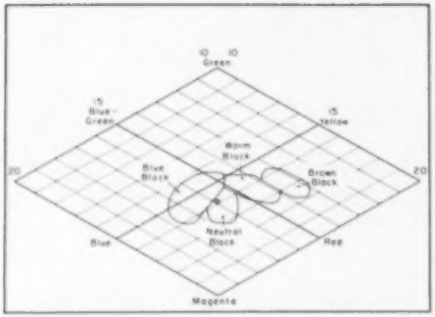


Fig. 6. Standardization of terminology can be based on measurement of tone.

center of the graph; that is, near neutral. Other samples, toned in various chemical toners, fall within the ranges shown. The fact that selenium toners produce samples which are generally in the reddish direction, compared with hypo alum tones, is clearly shown in Figure 5. It is also evident in Figure 5 that the same tones can be formed by some papers in hypo alum toner or by other papers in selenium toner. There are spaces on the charts shown in Figure 5 where no image tones have yet been recorded. This fact presents a challenge to chemists working on emulsion and processing variables that influence image tone. The measurement of image tone provides a useful tool to these chemists. By means of this tool, controlled chemical experiments can be made and the results plotted. Indication of variation in the proper direction can be easily read from such charts as Figure 4 or Figure 5 even though the magnitude of this change is not sufficient to be of practical importance.

Standardization of terminology can be based on measurement of tone. In the past, confusion has resulted when various manufacturers used different words to describe the same tone or used the same terms for dissimilar tones. The Eastman Kodak Company is now in the process of standardizing descriptive names of image tones produced by direct development with reference to measurements as shown in Fig. 6. The names Neutral Black, Blue Black, Warm Black, and Brown Black have been assigned to samples plotting within the tentative limits shown. Use of measurements referred to such a chart would make possible the establishment of uniform terminology throughout the photographic industry.

Dependence on Stock Tint

Measurements of image tone can be made in two fundamentally different ways. It is possible to make the readings relative to a fixed-out sample of the paper. This gives a determination of the image tone of the silver deposit independent of the color of the paper stock used. For some chemical and manufacturing problems this is the desired information. However, a value of image tone measured against a constant white standard correlates better with subjective impression of tone because the tone seen in a print depends somewhat upon the paper stock as well as the color of the silver deposit. If the same emulsion is coated on both a buff stock and on a white stock, the prints made on the buff stock paper will look decidedly warmer, particularly in the highlight region. Image tone measurements expressed relative to magnesium oxide correlate with this difference.

It is necessary to remember that the image tone measurement is strictly representative of only one density level. However experience has shown that relative differences between papers can be classified by their difference at this important level without appreciable error.

Conclusions

Measurement of image tone provides a useful tool for maintaining standardized production over a period of months. For such purposes visual examination is faulty because standards change somewhat with time and the memory of even skilled examiners is not sufficiently reliable to maintain constant production over long periods of time.

Measurement of image tone is also valuable in the search for new image tones by chemical development. Research on the effects on image tone of various processing chemicals and methods can be conducted in a more systematic manner by measurement of image tone. Image tone measurement will never replace the making of prints for visual examination in testing. In the last analysis, the photographer has to see what the difference is in order to know whether it is an important one or a pleasing difference. However image tone measurements can be applied successfully as a quality control technique after standards have been selected.

Experience over the past several years has shown that the system described herein is fast and precise and that the values obtained correlate well with visual examination.

1952 TECHNICAL PAPERS PROGRAM

The Chairman of the Program Committee for the Technical Division sessions at the 1952 national convention of the Society has issued an invitation for technical papers. To be assured of a place on the program, it has been requested that Titles and Abstracts reach the Chairman's hands by March 31st. This is earlier than the closing date in previous years because the convention, to be held in New York City, is scheduled for August (12th to 16th) instead of in October.

Sessions of interest to speakers on professional and scientific aspects of photography have been arranged as follows:

Symposium: Photography in Medicine and Biology

Symposium: Photography in Engineering and Science

PSA Clinic: Photographic Materials, Equipment, Processing

PSA Clinic Color Photography Materials and Methods

Technical Paper Session: Photographic Theory and Practice

Authors are requested to write directly to the Technical Division Program Committee Chairman, Hubert Scheffy, 343 State Street, Rochester 4, New York.

THE EFFECT OF OXYGEN AND MOISTURE UPON DESENSITIZATION IN PHOTOGRAPHIC EMULSIONS*

W. Vanselow, R. F. Quirk, and B. H. Carroll

ABSTRACT

The effect of oxygen upon the formation of the normal latent image of a motion-picture positive emulsion which had not been treated with a desensitizer was first investigated. Although oxygen did not influence latent-image formation, it did have a marked effect during the fixation of the emulsion or upon the latent image after the silver halide had been fixed out for physical development.

A set of four experimental coatings of a medium-speed bromoiodide emulsion, consisting of a control emulsion and three emulsions desensitized prior to coating, was studied in the presence of (a) oxygen and (b) nitrogen at 20 and 80 percent relative humidity. The results generally show an enhancement of desensitization, due to both sensitizing and desensitizing dyes, by oxygen and by increased humidity. While the effect of oxygen is in the direction predicted by Blau and Wambacher, it is small compared with the desensitization produced by some dyes themselves. The data indicate strongly that these dyes alone are capable of desensitization: If they desensitize by an oxidation process, regeneration of dye by oxygen might be expected to increase the effect.

THE effect of oxygen and moisture upon desensitization in photographic emulsions has been discussed at various times in the literature.

Blau and Wambacher[1] found that the silver grains marking proton tracks in photographic plates appeared after development only when the plate had been treated with pinakryptol yellow or some similar substance, and when the exposure to the particles was carried out in air at reduced pressure or in nitrogen. They investigated the effect of light on photographic emulsions similarly desensitized and exposed in air at different pressures of different gases. They found that: (1) The desensitization is much reduced by reduction of the air pressure and by substitution of pure nitrogen for air. (2) The effect of oxygen is not as marked when the plate is moist. (3) The effect is apparent with pinakryptol yellow, desensitol, indulin scarlet, phenosafranin, a mixture of pinakryptol yellow and indulin scarlet, antilumen, and pinakryptol, but not with pinaflavol. (4) Reduced pressure has no influence on plates not desensitized by one of the substances mentioned.

That this effect was not noticed by Sihvonen[2] in silver bromide sols is probably due to essential differences in the experimental conditions. On the basis of their results, Blau and Wambacher concluded that the dye itself plays only an auxiliary part, probably that of a catalyst, in the desensitization process, the major part being played by the oxygen of the air. These results appear to support the well-known oxidation theory of desensitization attributed to Lüppo-Cramer. Blau and Wambacher[3] discussed the influence of atmospheric oxygen and of the desensitizer concentration on the sensitivity of desensitized photographic layers. They conclude that the facts of desensitization are best explained by an oxidation theory, according to which the desensitizing dye acts as an intermediary between the oxygen of the air and the development nuclei produced by light.

Inasmuch as the entire experiment was carried out in either nitrogen or oxygen, an apparatus such as that shown diagrammatically in Figure 1 was used.* All solutions required for processing the film were also treated, before the experiment was begun, with either nitrogen or oxygen, as the case required. Briefly, the assembly consisted of

* Communication Number 1451 from the Kodak Research Laboratories, Rochester 4, New York. Received 26 October 1951.

* The apparatus was an outcome of a similar one designed earlier for another experiment by Drs. T. H. James and W. Vanselow.

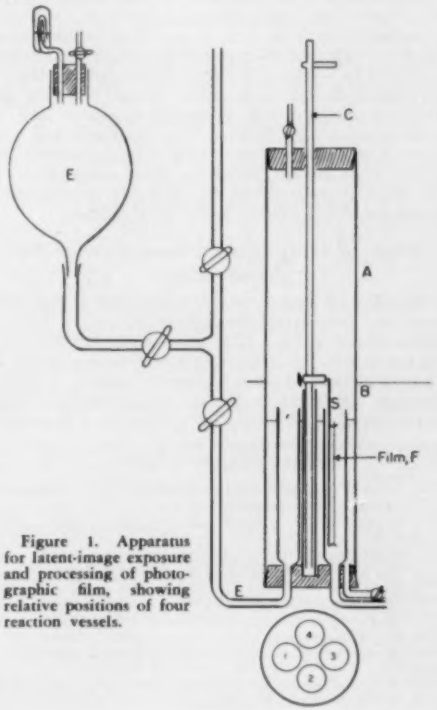


Figure 1. Apparatus for latent-image exposure and processing of photographic film, showing relative positions of four reaction vessels.

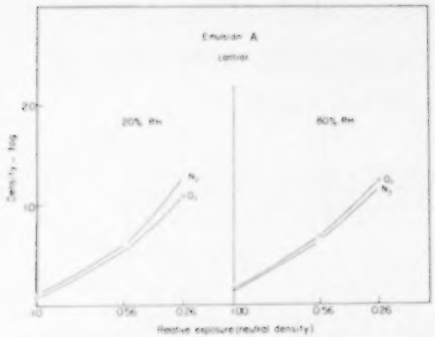


Figure 2. EMULSION A—control
Density-fog *vs.* relative exposure plots at 20 and 80 percent relative humidity for N_2 (nitrogen) and O_2 (oxygen) treatments of films. Four-minute development in D-16.

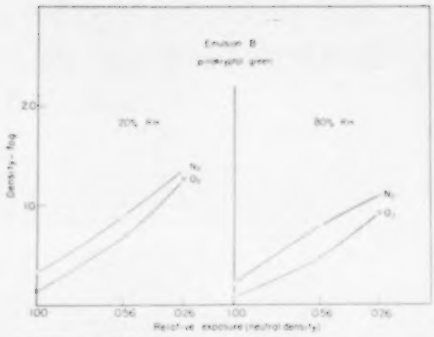


Figure 3. EMULSION B—pinakryptol green
Density-fog *vs.* relative exposure plots at 20 and 80 percent relative humidity for N_2 (nitrogen) and O_2 (oxygen) treatments of films. Four-minute development in D-16.

four units, designated by E in Figure 1. The film F is fastened to its support S and rod C by means of which it can be lowered into and removed from the various solutions. Usually, there were three processing solutions, i.e., developer, water, and hypo. The extra tube allowed for a possible extra operation, such as pretreatment of the film. These four tubes, containing processing solutions, are numbered endwise, 1, 2, 3, and 4, at the bottom of Figure 1. A guide at the top of the assembly A permitted the film to be rotated and guided in the dark to the position desired. The film was exposed to light when the film was raised above point B. If nitrogen was to be used, all air and oxygen were removed from the system and from the solutions in the E tubes before the experiment was started. After fixation, following direct development, or after physical development, the film was removed from the apparatus and washed in the usual manner.

Effect of Oxygen upon Formation of the Latent Image

The effect of oxygen upon the formation of the latent image was investigated first. A sample of an Eastman Motion Picture Positive Film, Type 3301, was introduced into the system. Exposure to light was made after the air had been replaced by either nitrogen or oxygen, as desired. The light source was a 25-watt tungsten-filament lamp, placed behind a 2.5-cm square aperture at a distance of 100 cm from the film. A neutral density filter of 0.26 density was inserted in the light path. Fixation, washing, and physical development* were all conducted in a controlled atmosphere. The experiments and results are listed in Table I. Oxygen, under the present set of conditions, did not influence latent-image formation. Oxygen, however, has a marked effect upon fixation or upon the latent image after the silver halide has been fixed out.

* Physical Developer Formula

Part A		
p-Phenylenediamine dihydrochloride	11.04	grams
Sodium sulfite (desiccated)	20.0	grams
Water	320	cc
Part B		
Silver nitrate	12.0	grams
Water	140	cc
Part C		
Sodium sulfite (desiccated)	288	grams
Water	1300	cc
0.1 *M* Borax	160	cc

Part B was added to Part C when both were completely in solution.

Part A was added directly before use. Development was carried on for two hours with nitrogen agitation.

Effect of Oxygen and Moisture upon Medium-Speed Bromoiodide Emulsions Desensitized Prior to Coating

A set of four experimental motion-picture positive emulsions was studied. In each case, except for the control emulsion, a sensitizing or desensitizing dye was added to the emulsion before coating and drying. Exposure conditions differed for each emulsion, the desensitized emulsions requiring considerably more exposure. All four emulsions were exposed at 75 cm from the light source.

A, the control containing no dye, was exposed for 0.5 second to a 25-watt tungsten-filament lamp with a neutral density filter of 0.52 in its path.

B was desensitized with pinakryptol green. Exposures of five minutes to the 25-watt lamp were used.

C was desensitized with 3,3′-diethyl-8,9-diazothiacarbocyanine iodide. This dye showed a large oxygen effect in experiments by J. Spence,[4] of these Laboratories, under conditions in which pinakryptol green desensitization was relatively independent of oxygen concentration. This emulsion exhibits a Herschel effect, and a Kodak Wratten Filter, No. 47, plus a cupric chloride filter, were used in the light path from a 60-watt tungsten-filament lamp. The exposure time was 20 minutes.

D was sensitized with 3,3′-diethyl-4,4′-diphenylthiazolocarbocyanine iodide. This dye is a moderate panchromatic sensitizer but simultaneously desensitizes quite strongly.[5] Wratten Filters No. 47 and 35 were used. Exposure times were five minutes to a 250-watt tungsten-filament lamp.

Briefly, the experiment consisted in holding the film in the desired gas (nitrogen or oxygen) at room temperature (25C) and at either 20 or 80 percent relative hu-

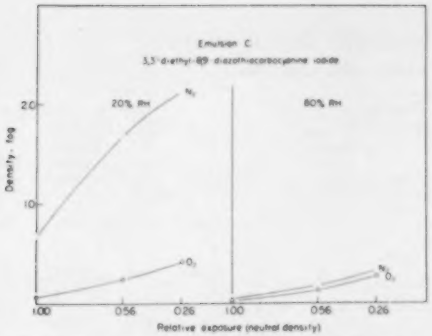


Figure 4. EMULSION C—3,3′-diethyl-8,9′-diazothiacarbocyanine iodide.
Density-fog *vs.* relative exposure plots at 20 and 80 percent relative humidity for N_2 (nitrogen) and O_2 (oxygen) treatments of films. Four-minute development in D-16.

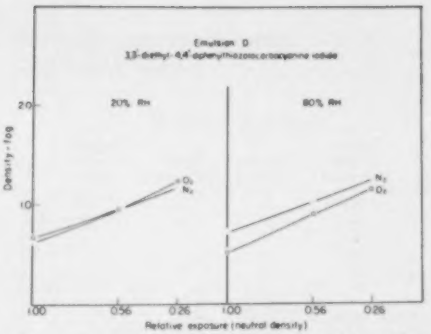


Figure 5. EMULSION D—3,3′-diethyl-4,4′-diphenylthiazolocarbocyanine iodide.
Density-fog *vs.* relative exposure plots at 20 and 80 percent relative humidity for N_2 (nitrogen) and O_2 (oxygen) treatments of films. Four-minute development in D-16.

midity for 65 to 70 hours, then exposing it to the intensity-scale sensitometer in the presence of the gas, developing it in the developer which had been previously deaerated with nitrogen in all experiments, rinsing in deaerated water, and fixing in deaerated hypo. All operations were carried on in the enclosed apparatus shown in Figure 1.

The sensitometer consisted of a tungsten-filament lamp, 25, 60, or 250 watts as required for each emulsion, placed 75 cm from the film. The lamp was housed in a lighttight compartment equipped with a shutter and a 2.5-cm square aperture. When required, a neutral density filter was used in front of the shutter. The step tablet was fitted around the upper section of the tube **A** in Figure 1 and consisted of three bands of neutral density film, each 4.5 cm wide and having densities of 0.26, 0.52, and 1.0. The entire equipment was operated in a room in total darkness.

The densities for the three steps of the wedge and for fog for the four emulsions, using a 10-minute development in Kodak Developer SD-21,* are listed in Table II. These data were obtained at 20 percent relative humidity in (a) nitrogen or (b) oxygen. The density ratios of oxygen to nitrogen are also listed. The oxygen had almost as much effect upon the control emulsion, **A**, as it had upon the desensitized, **B**, emulsion. This feature was further investigated through the use of a more energetic developer, i.e., Kodak Developer D-16.* As Spence had observed earlier, 3,3′-diethyl-8,9-diazothiacarbocyanine iodide showed a large oxygen effect. Emulsion **D** showed little difference with nitrogen and oxygen treatments.

The four emulsions were studied in the presence of nitrogen and oxygen at 20 and 80 percent relative humidity using four minutes' development in D-16.

* Composition of Kodak Developer SD-21

Elon	2.0	grams
Hydroquinone	5.0	grams
Sodium sulfite (desiccated)	100.0	grams
Potassium bromide	0.25	gram
Borax	8.0	grams
Boric acid	8.0	grams
Water to make	1000	cc

Table II

(20 Percent Relative Humidity)

Emulsion	A		B		C		D	
	N	O	N	O	N	O	N	O
	Densities, Observed							
Development,								
10 min. in	1.16	0.88	1.37	1.01	1.62	0.40	0.48	0.51
SD-21	0.73	0.48	0.96	0.60	1.19	0.25	0.38	0.39
	0.25	0.15	0.45	0.21	0.50	0.08	0.26	0.25
Fogs	0.11	0.08	0.12	0.07	0.06	0.03	0.13	0.10
	Ratios of Densities—Oxygen : Nitrogen							
	1.00 : 0.75		1.00 : 0.73		1.00 : 0.25		1.00 : 1.05	
	0.66		0.63		0.21		1.01	
	0.60		0.47		0.17		0.98	
Fogs	0.73		0.58		0.58		0.76	
	Ratios of Densities (corrected for fog)							
	1.00 : 0.77		1.00 : 0.75		1.00 : 0.23		1.00 : 1.15	
	0.66		0.62		0.19		1.13	
	0.50		0.40		0.11		1.19	

In general, the change in development did not alter the previous conclusions. Within certain limits, the results for the experiments carried out at 20 percent and 80 percent relative humidity are parallel except for **C**, the emulsion desensitized with 3,3′-diethyl-8,9-diazothiacarbocyanine iodide. At 80 percent relative humidity, its speed has dropped to nearly that at 20 percent relative humidity but the effect of oxygen at 80 percent was practically the same as at 20 percent relative humidity. Figures 2 to 5 show values of density minus fog plotted against relative exposure for the four emulsions at the two humidities and in the presence of nitrogen or oxygen.

* Composition of Kodak Developer D-16

Elon	0.3	gram
Hydroquinone	6.0	grams
Sodium sulfite (desiccated)	38.0	grams
Sodium bisulfite	1.2	grams
Sodium carbonate (desiccated)	19.0	grams
Potassium bromide	0.9	gram
Citric acid	0.7	gram
Water to make	1000	cc

Table I

EFFECT OF OXYGEN ON LATENT-IMAGE FORMATION AND ON FIXATION

Emulsion: Eastman Motion Picture Positive Film, Type 3301

No.	Operations in Presence of				A Density Exposure, 30 sec.			B Density Exposure, 300 sec.			Ratio B/A
	Latent-Image Formation	Fixation (5 min.)	Wash (30 min.)	Physical Development	Density	Fog	Density Minus Fog	Density	Fog	Density Minus Fog	
1	N	N	N	N	0.24	0.09	0.15				
6	N	N	N	N				1.00	0.08	0.92	6.1
2	O	N	N	N	0.20	0.07	0.13				
7	O	N	N	N				1.02	0.08	0.94	7.2
3	N	O	N	N	0.13	0.07	0.06				
8	N	O	N	N				0.40	0.06	0.34	5.7
4	O	O	N	N	0.10	0.07	0.03				
9	O	O	N	N				0.26	0.04	0.22	7.3

To summarize, the influence of oxygen on the desensitization of the emulsions was as follows:

The desensitizing action of pinakryptol green was enhanced in the presence of oxygen at both 20 percent and 80 percent relative humidity.

The desensitizing action of 3,3'-diethyl-8,9-diazothiacarbocyanine iodide was greatly enhanced by oxygen at 20 percent relative humidity. At 80 percent relative humidity, however, it was no more effective in oxygen than in nitrogen. The desensitizing action of 3,3'-diethyl-4,4'-diphenylthiazolocarbocyanine iodide at 20 percent relative humidity was about the same in oxygen and nitrogen; at 80 percent relative humidity, it was greater in oxygen.

The results generally show an enhancement of desensitization by oxygen, and by increased humidity. There was strong desensitization by each of the dyes in the absence of oxygen, and the enhancement by oxygen was small compared to the total desensitization. The data indicate that oxygen is not necessary to desensitization. Regeneration of the dye by oxygen may contribute, as would be expected if desensitization is an oxidative process and only those molecules immediately adjacent to sensitivity nuclei are able to take part.

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Equipment and Technique for Molding Spherically-Curved Film

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SUMMARY

Commercial heavy base sheet photographic film has been molded spherically to a radius of curvature of eight inches by means of a pressure-diaphragm, radiant heater method with complete success. The molding operation has been carried out routinely for several months in Las Cruces, New Mexico, where the Super Schmidt meteor cameras are being used.

A HIGH-SPEED, wide-angle camera was required to photograph meteors and the trains of incandescent material left behind as they streak through the sky, in connection with an investigation of meteor phenomena by the Harvard College Observatory. For this purpose Dr. James G. Baker designed a unique camera, a number of which are being built by the Perkin-Elmer Corporation. For a full description the reader is referred to Sky and Telescope, Volume 8, Number 4, 1949. The optical characteristics of the new camera are unique. They involve an aperture of 12¼ inches, a focal length of 8.0 inches, an optical focal ratio f/0.65, and an effective field of 55° without appreciable vignetting at the edges. Actually, the interposition of the film in the optical path reduces the effective aperture to f/0.81. One compromise necessary in the design of these

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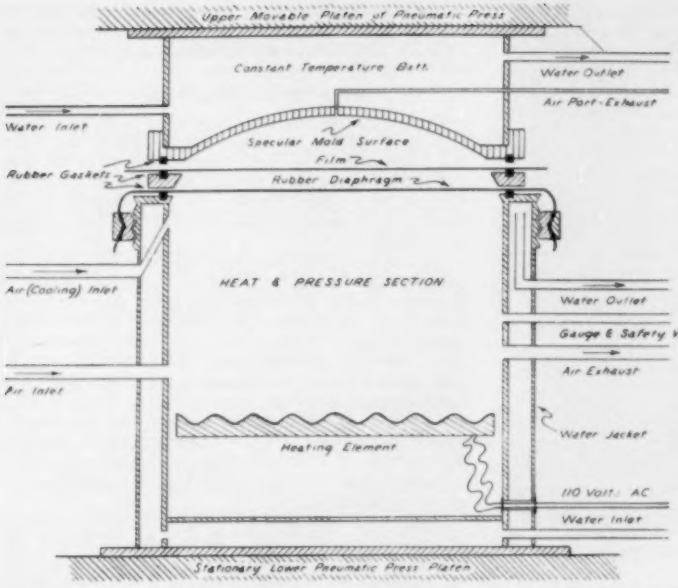

Fig. 2. Schematic diagram of the film molding machine in which ordinary heavy base sheet film is molded to a semi-permanent disc in 90 seconds. After a heating period of 15 seconds, a pressure of 10 pounds/square inch gives satisfactory results if followed by a 30 seconds cooling period using a blast of compressed air. The 2000 watt radiant heater produces a slight, overall fog on the film by radiation through the gum rubber diaphragm but this does not hinder use of the film for recording the paths of meteors.

fast cameras is the extreme curvature of the focal curve. Flattening this focal surface, although desirable, would complicate the optical system unduly. As a consequence, the focal curve of the Super-Schmidt meteor camera is a spherical section with a radius of curvature of 8.0 inches and chordal diameter 7.4 inches. A diagram of the camera optics is shown in Figure 1.

The optical tolerances of the focal surface for the cameras are unusually critical because of the extreme focal ratio of f/0.65. To preserve image quality it is thus necessary to maintain the photographic emulsion on the surface of the required sphere within a tolerance of 0.0005 inches. An ideal focal surface would be a molded glass or plastic shell with the photographic emulsion on the convex surface. This solution to the problem is not a practical one because of the expense of such shells and because of the difficulty in coating the emulsion evenly on convex surfaces.

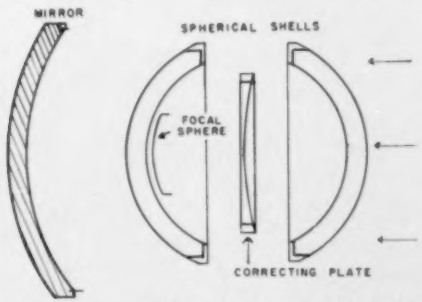

Fig. 1. Schematic diagram of the Super-Schmidt Meteor Camera.

Accordingly, preliminary experiments were made to determine the feasibility of curving ordinary sheet films to the required shape. These preliminary investigations, made by the Eastman Kodak Company, demonstrated the practicability of film molding, and on the basis of information thus obtained we undertook the design of production equipment and techniques for molding the films to be used in the new cameras. It is believed that the apparatus, processing procedures, and performance data which we developed would be useful to anyone desiring to undertake film molding for other applications.

Design and Construction of Molding Equipment

After extensive experiments and several preliminary models, the film-molding machine schematically portrayed in Figure 2 was developed. It consists of a lower pressure section and a rigid upper section, the mold. A heating element is located in the bottom of the pressure section. Stretched across the top of the pressure section is a rubber diaphragm. The upper chamber containing the molding surface is cooled by circulating water through the confined space above the mold. The sheet film is laid between the top and bottom sections, emulsion up, and gripped by rubber gaskets to effect a pressure seal as the two sections are clamped together. The film-molding operation then consists of the heating period, the molding period in which the film is forced against the mold by air pressure, the setting period, the cooling period, and finally the removal of the film from the machine to the cutter for edge-trimming to the prescribed size. The entire molding cycle is supervised by an adjustable automatic timer used to regulate the heating period and to activate the solenoid valves

controlling water and air flow. Emphasis was placed upon simplicity of operation and maintenance, and upon the utilization of water, electricity, and compressed air.

The Mold

The dome of the concave mold of the present model was machined from a forged copper pancake 2 inches thick by 12 inches in diameter. After the rough cutting and grinding had been completed, the dome was ready for final polishing. The surface was to be finished to a tolerance of ± 0.0005 inches. A lap was made with glass discs embedded in plaster-of-paris—the lap being set or formed on the greased mold itself. An optical grinding compound was then used with the lap to rough-polish the mold. Kerosene was added to the powder making a fluid polishing paste. This was designed to avoid *charging* of the copper surface, to prevent the embedding of the minute compound particles in the relatively soft copper. Some charging, nevertheless, did take place. The embedded particles of grinding compound were pulled out of the copper during the buffing process, causing minute scratches. These could not be tolerated in the finished product and, as a consequence, the buffing period was greatly lengthened. The final polishing before plating was done with a jewelers' rouge and a buffing wheel exclusively. The chromium electroplating process consisted of thin layers of copper, then nickel and then chromium being deposited upon the prepared surface. These layers are several ten-thousandths of an inch thick.

Subsequently, the thermal properties of copper have been found to be unnecessary, and equally satisfactory molds have been made using steel and slightly different grinding and polishing operations.

Kettle, Floating Ring and Diaphragm Holder

The kettle is the lower chamber or pressure section of the production equipment and houses the radiant heater. Construction of the kettle and its enclosing jacket is of stainless steel. This provides space for a circulating constant-temperature water bath. Openings to the inner air chamber must be provided for the two air inlets, the air exhaust, the heater connections, the gauge and safety valve. Openings to the outer jacket must include the water input and water outlet with internal provisions for circulation of water beneath the kettle.

The floating ring upon which the film rests is the thin unit between the dome and the rubber diaphragm (see Figure 3). The purpose of the ring is to provide more uniform heating, which is primarily conduction from the diaphragm, for the photographic film. Air exhaust holes in the ring assure complete contact of the film and diaphragm. Furthermore, the ring separates the two during the period in which the diaphragm is being heated. When the air exhaust valve has been closed and the air input opened, the contact is effectively simultaneous over the film surface.

The diaphragm holder (see Figure 3) consists of two parts: the inner component leads onto the kettle; the outer component, which is split, spreads over the diaphragm and inner component. The diaphragm is held in place between the two, the split section being drawn down on the rubber by means of a clamp. The diaphragm may then be stretched taut over the kettle by turning the threaded holder assembly. Notice that the downward pressure of the pneumatic press, coupled with the gasket compression, affords the final airtight seal between chambers.

Film Molding Press

The purpose of the pneumatic press is to provide an aligned mount for the dome and the kettle—the dome being mounted on the upper movable platen of the press and the kettle on the stationary lower platen. When the film has been placed between the dome and kettle, the press is closed, firmly holding the film in place and sealing the system.

The radiant heater rests on a platform with three adjustable legs. In this way, the distance from heater to diaphragm can be set at any distance less than 8.0 inches. Several types of heaters have been tried, the one finally adopted being a Universal open-type heater, Model 1200. It is a two-coil, 2000 watt unit, 9 inches in diameter. The coils are used in parallel. Because a gum rubber diaphragm is not completely opaque, some red light from the open heating coils fogs the film to a slight but even degree. Should the slight fogging of the film be a serious disadvantage in types of work other than meteor photography, it is probable that an infrared absorbing filter could be employed satisfactorily.

Closed units have also been tested, commercial coil units enclosed in cast steel boxes. These have the serious disadvantages that accompany high heat capacity units. Satisfactory results can be obtained, but the cycle is more critical, especially with respect to the allowable range of time between cycles. This results from the continued heating of the diaphragm for many minutes after the cycle is completed.

The Cycle Timer

The molding operation and the time between cycles must be accurately controlled if thermal equilibrium of the apparatus is to be reached and maintained.

Basically the timing device consists of a synchronous motor geared to a shaft on which turn six individually adjustable cams. These cams operate microswitches (see Figure 3) which in turn activate the solenoid valves con-

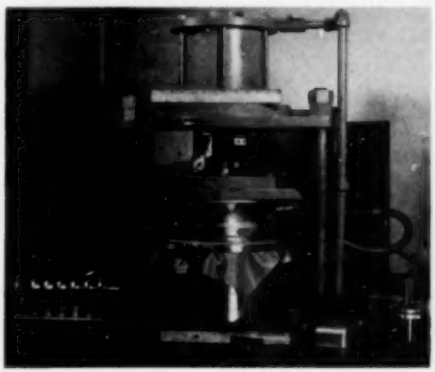

Fig. 3. Photograph of the film-molding machine.

trolling (a) the air input, (b) the jet or cooling air input, and (c) the air exhaust; the two-way double solenoid valve controlling (d) the downward action of the pneumatic press and (e) the upward action of the pneumatic press; (f) the 2000-watt radiant heater; (g) the overall time of a single cycle.

With lights out, the film is placed in position between kettle and dome. When momentary toggle switches are depressed, one with each hand so as to avoid crushing fingers, the press closes and the cycle is started. After about 90 seconds, the press is automatically raised and the operator moves the molded film to the cutter and "reloads" the molding machine. The next cycle can be begun by activating the dual toggle switches anytime after the cam-operated microswitch has reversed, indicating that the heating unit is back to working temperature.

The Film Cutter

The film cutter is used to trim the 10″ x 10″ sheet film to the required circular cross section after it has been removed from the molding machine. The cutter consists of three components—the punch, the die and the pneumatic press which activates the punch.

The die hole is in the base plate of the press and is so arranged that the cut film drops directly from the cutter into the storage cans. The upper, movable, platen contains the punch, encircled by a spring-loading ring which presses the unmolded flat part of the film to the base plate just before and during the cutting process.

Performance Tests of Molded Films

While developing the film molding machine, a number of problems were investigated and various tests performed whose results would be useful in connection with any similar work involving the molding of photographic film. Accordingly, some of this information is recorded as a matter of general interest in the following paragraphs.

Temperature Effects. Standard emulsions molded at temperatures as high as 220 F do not show any impairment of photographic quality for exposures made either prior to or after the molding process.

Pressure Effects. The moderate pressures of less than 20 lbs/sq in used in this apparatus do not seem to produce any deleterious effect on the film. However, considerable difficulty with earlier models was experienced because of minute surface imperfections in the surface of the mold, which produced a pattern in the developed image of densities as high as 0.1. It is, in part, for this reason that the surface of the mold must be prepared with such elaborate care.

Variation in Thickness. Because of the critical importance of precise focus in the operation of the Super-Schmidt meteor cameras, careful measurements were made of the film thicknesses before and after molding. The edge-to-center difference in thickness for identical molding cycles was found to be uniform and approximately 0.0006 inches for three commonly-used films. Since the focus of the Super-Schmidt cameras is critical to about 0.0005 inches, the fact that the curved films are 0.0006 inches thicker at the edge than at the center must be compensated for in designing the film holders.

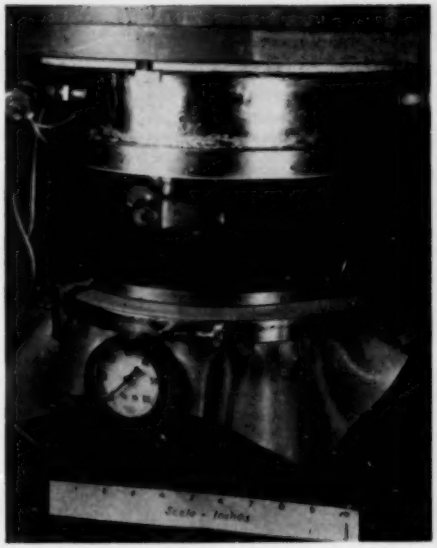

Fig. 4. Closeup view of the floating ring and diaphragm holder.

Distortion. To date no measurements have been made of the degree of distortion in molded films introduced by the processing of the molded photographic emulsion. The lack of required precision optical equipment has made these tests impossible. However, there are grounds for belief that systematic distortion on the final glass positive should be less than on photographs produced directly by more conventional wide-angle cameras, provided the films are copied within a few weeks from the time of processing.

The Permanence of Curvature. Although the process employed in curving film has been termed a "molding process," this is not quite correct. The name implies a *permanent set* of the film rather than the semi-permanent *distortion* which is actually imparted. No attempts have been made to mold film to a permanent set. It is doubtful if this would be successful below temperatures of 150 C, the point at which cellulose acetate begins to soften and a point well above the limits where the photographic gelatin will be seriously softened and sensitized. Furthermore, because of the small rate of relaxation in film produced by the present method, the attempt to set the film permanently was unnecessary.

If it were not for the indeterminate method in which the film surface stretches and relaxes—and the accompanying errors in measuring positions on the developed film—it would be conceivable that flat film could be distorted to the proper shape *after* it was placed in the camera. One pound/in^2 pressure is sufficient for this distortion when the film is at room temperature. However, because of localized distortion with relaxation of curvature, bending the film in the camera was not feasible. For pre-molded film, it is necessary that its shape does not change enough to re-

quire more than a slight pressure to make it conform to the film holder in the camera.

In order to obtain some estimate of the rate of increase of curvature with time, films were forced into a constant-temperature mold (temperature ranging from 25-60 C) and held there for varying periods of time (10 seconds to 10 minutes). The ensuing change of radius of curvature was then measured during a period of from one to 24 hours after molding.

From these measures, the following approximate relationships were found. The constancy of the results was not good and they can be used only for general insight into distortion and molding problems and not for quantitative extrapolations into the time and temperature range utilized in the actual molding process.

(1) The measured radius of curvature in every case was approximately linear with respect to the logarithm of the time elapsed since molding. The rate of decay remained nearly constant for periods of time great enough, in the case of film molded at low temperatures, for the film to return nearly to its original flatness; or, for film molded at high temperatures, for the film to reach a point of stability where the change could not be detected in a matter of hours.

(2) The rate of decay was strongly dependent upon molding temperature—the logarithmic rate of decay doubling for each 10 C decrease in molding temperature for film produced with 10 minute periods. This relationship holds for temperatures from 24 C to 58 C.

(3) The rate of decay was measurably dependent upon molding times (i.e., the period during which the film was distorted and maintained against the constant temperature mold) for a molding temperature of 50 C. For lower temperatures the molding time appeared to be relatively unimportant. This is possibly an indication that some of the curvature at higher temperatures is a result of true molding, whereas the remainder is a temporary distortion due to the stretching of the film. If this is the case, the curvature of films molded by the present process should decrease to a certain minimum value and remain there. Because the quantitative results of the above experiments were not of sufficient accuracy to show this, it may only be demonstrable to be the case after film has been stored for a very considerable period. For an approximation of this value, a few films were stored for six months at room temperature and it was found that the radius of curvature had changed by approximately ¼-inch.

In the early attempts to obtain satisfactory curvature, several other relaxation effects were noted.

The molding period, the time during which the heated film remains forced against the mold before cooling, should be approximately 15 seconds. Too short a setting period results in a more rapid relaxation of curvature. The cooling period, during which compressed air is sprayed through the lower chamber while the pressure on the film is maintained, must be long enough to assure that the film has again become rigid. For best results a cooling period of no less than 30 seconds should be used.

Molding pressures affect the curvature only slightly within a range of pressures from 5 to 30 pounds/in². A pressure of 10 pounds/in² is quite satisfactory.

Storage in locations subject to wide temperature and humidity variations, especially where extreme cold is encountered, results in a random curling of the film.

Film Support in the Meteor Camera

The shape of the focal surface in the camera is determined by the film holder—an approximately-spherical section of aluminum of slightly greater chordal diameter than the molded film and of shape such that the variations of film thickness will be accurately corrected when the film is drawn down to the plate holder. Vacuum, applied to the back of the plate holder, reaches the front surface through a 1/32 inch hole in the center of the holder. It was first hoped that the slight roughness of the film holder surface would be sufficient to allow the vacuum to act efficiently over the entire surface. In most instances this was satisfactory for newly-molded film but as it began to lose its curvature, a few hours often being sufficient, more rubbing and pressing of the film was necessary to force it to the surface. After a still longer period of time, it became impossible to bring the entire area of the film to the surface of the holder. Small patches, of about one square inch, remained—"high" by several thousandths of an inch.

To overcome these difficulties, grooves radiating from the center hole and others concentric with the holder were scratched into the aluminum. These supplied the necessary air channels but it was found that depth of the lines had to be carefully controlled in order to assure their being deep enough to be effective but not so deep that the film would be pulled down into them. If the latter effect takes place, it is probably possible to reproduce the pattern of the grooves on the exposed film as long, narrow areas of out-of-focus images. The grooves are approximately 0.002 inches wide and deep. They extend to within ½ inch of the edge of the holder and divide the remaining area in roughly equal parts. About 100 inches of scribe lines are used on each holder.

With this method of support, it has not been possible to discern any central portions of the film which deviate from the focal surface by more than 0.0005 inches. A slightly turned-up lip at the extreme edge (3/16-inch) of the film is not affected by any of the methods yet devised.

Handling and Processing Problems

Molded film has a strong tendency to curl and to pucker in areas (especially at the edge) during development if its edge is not restrained to approximately a plane. This requirement, and the accentuated problems of uniform development with curved films, demanded special processing equipment for holding the films in individual racks. In order to avoid emulsion abrasion or scratching, similar racks, which are simply plastic rings, are used to transport the films in light-tight containers.

BIOCHEMISTRY AND PHOTOGRAPHY

F. W. H. MUELLER*

SINCE early days the photographic industry has relied rather heavily for its raw materials on organic products of nature not only to impart to inorganic silver salts optimal photographic sensitivity but also to provide a flexible, dimensionally stable support for the modern film. As in other fields of applied chemistry, the trend to develop synthetic substitutes often specifically tailored to a certain requirement has been increasing in photographic manufacture in recent years. While the time-honored use of gelatin as a dispersing agent for the silver salt, and the use of cellulose derivatives for filmbase may continue for quite some years, it is evident that in the photographic research laboratories chemists are experimenting to free themselves from exactly those products of nature which proved to be invaluable in the first 100 years of photography. Yet, the number of biochemical materials used to modify emulsion and film base properties is truly amazing. The initiated know that nature was our teacher and is still guiding us along to the road of further progress.

When the author, who received his early training in protein and biochemistry, joined the photographic industry a good number of years ago, he found himself "at home," particularly in the field of emulsion-making, after only a brief study of the photographic literature then in existence. The role of proteins was already recognized to be important. Photographic journals and patent literature contained many references to cystine compounds. The use of carbohydrates, bile salts, milk, fats, waxes, amines, alkaloids, tannin, shellac, and lignin for photographic uses had been practiced or advocated. When vitamins and hormones came along, it wasn't surprising to find that these even biochemical substances also attracted the interest of the photographic chemist.

It cannot be within the scope of this paper to unravel the details of the photographic usefulness or the photographic effects of these natural products, even though it would make a fascinating story. However a few examples will illustrate how nature provided invaluable guidance.

The unique properties of gelatin and its peculiar sensitizing effect on silver halide had been recognized over 80 years ago. Scientifically the often uncontrollable properties of gelatin remained little understood until about 30 years ago when, mainly in the laboratories of the Eastman Kodak Company in the United States and the Agfa organization in Germany, the results of fundamental studies began to lift the veil of mystery from gelatin. The biochemists may be interested in following how this was done. Punnett[1] began by adding "biochemical extracts" prepared from animal or vegetable tissues and Sheppard[2] ended up after years of research with the isolation of allyl isothiocyanate as a sensitizing agent responsible for the so-called "ripening effect of gelatin." This discovery prepared the way to the Gurney and Mott theory of the silver sulfide sensitivity speck in latent image formation. Studies of the gelatin manufacturing processes and conditions by Agfa, in particular the investigation of protein degradation during the liming treatment of animal matter for gelatin production, likewise led to sulfur-containing substances, the polythionates, and their use as sensitizers[3]. The variety of raw materials used for gelatin—hides, bones, sinews, cartilage, horn—as well as the age of the animal, its fodder, and the subsequent processing conditions, amply explain and account for the conflicting statements in the literature.

Academic studies by Max Bergmann[4] and Michaelis[5] on the alkaline decomposition of keratins and proteins supplemented and supported the findings in industrial laboratories. It soon became evident that many sulfur-containing compounds possessing the proper degree of sulfur lability were useful sensitizers in gelatin so suitable sulfur compounds were extensively studied. The redox system of cystine was investigated by Steigmann who also suggested glutathione as a sensitizer in 1926 as well as methionine, as a sensitizer in silver chloride emulsions, in 1946[6,7].

After the role of sulfur sensitizers in gelatin had been partially clarified in the late twenties, emulsion chemists had to realize that the function of gelatin in photography was not yet fully understood. Important so-called anti-sensitizers or restraining compounds were found in gelatin by various investigators. These restrainers retard the growth in size of the silver halide crystals or slow down the formation of sensitivity specks or may be useful in inhibiting fog. Their chemical nature and their mode of action and their origin have not yet been completely elucidated. Research during the last fifteen years, however, has provided some information. It appears that several classes of restrainers may occur in natural gelatin just as several different types of sulfur compounds could be found. There are high molecular weight restrainers, perhaps polypeptides, and there are low molecular weight heterocyclic compounds similar to synthetic, insoluble, silver salt forming compounds first patented by Agfa[8]. Steigmann believes that thiazolidinecarboxylic acid derived from cystine may fall into the latter class[7]. Amino acids such as arginine and histidine also act as restrainers due to the formation of silver complex salts on the silver halide surface[9].

Lüppo-Cramer first referred to the retardation of the growth of silver halide crystals by high molecular weight protein products, such as albumen and others. Hydrolized keratin, serum albumen and globulins, when added to gelatin, somewhat resemble natural restrainers in their effect, although they are not identical in photographic effects with natural restrainers. Early Agfa patents[10] pertaining to alkaline or enzymatic protein hydrolysates described sensitivity and clearness improvements obtained by such additions which undoubtedly exemplify the action of high molecular weight restrainers. Some manufacturers prepared restrainers from structural proteins such as hair, feathers, fish scales, edestin, etc. More recently Rousselot[11] expressed the opinion that some restrainers do not contain sulfur. The Agfa work during 1941-42[12] led to the isolation of tetranucleoproteids from gelatin. It is of interest to note that prior to this work, purines, pyrimidines—as a matter of fact all decomposition products of nucleic acids, had been patented by several photographic manufacturers as emulsion stabilizers. Incidentally, the Agfa work on nucleic acid has more recently been confirmed in the Ansco Laboratories by R. Conant (unpublished). Aside from the described restraining effects of some of the protein products, a number of proteins such as peptone, prolamines, (zein, gliadin, etc.) have found auxiliary uses in the photographic manufacturing technique.

Reviewing the use of carbohydrates in photographic emulsions, it may be stated that their fog producing chemical effect on silver halide emulsions (which may involve reduction through the aldehyde group) is undesirable, although pentoses and hexoses have been utilized in hardening gelatin emulsions. Steigmann[13] found that some gelatins contain amino sugars or aldehydes derived from mucopolysaccharides in the raw material. Sugar was employed in early emulsion making methods. Dextrin, agar, starch, and pectin are described as gelatin extenders, substitutes, or matting agents. Sorbitol acts as a humectant. Salts of polyglycuronic acid (alginates) and vegetable gums were suggested as stripping film adhesives[14] and chitin, a glycosamine containing polysaccharide, is specified in antistatic layers[15]. In most of these applications it appears that the physical rather than the chemical properties of carbohydrates have been found useful.

The earlier use of fat (in the form of vegetable oils) or of milk as a surface matting agent is hardly practiced any more. However, the introduction of non-diffusing color formers as used in the Agfa Color and the Ansco Color processes brought back the chemistry of long chain fatty acids, of the type occurring in coconut oil, into the realm of the photographic chemist. The method of Eggert, and later of Froelich and Schneider, of dispersing "fat-tail" color formers with bile salts is again an obvious parallel to a biochemical process[16]. Lecithin—a phosphatide—has been described as a stabilizer[17].

In the field of antihalation dyes, photographic chemists usually look for dyes which can easily be destroyed in the photographic processing solutions. Since nature provides some classes of rather unstable dyes, it isn't surprising that pyrrilium and xanthylium

* Ansco Research Laboratory, Binghamton, N. Y. Received 14 September 1951.

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salts were introduced by Thompson[19]. Similarly, murexide, the ammonium salt of purpuric acid[19] was also proposed. Wilmanns utilized the colored copper protein complex, familiar to the biochemist through the Biuret reaction, as an antihalation "dye"[20]. It appears however that these latter applications have not gained much commercial importance.

Certain vegetable dyes impart orthochromatic and panchromatic spectral sensitivity to silver halide. J. M. Eder[21] lists chlorophyll, curcumine, carotene and others, as well as the blood "dye," hematoporphyrine. They do not compete in efficiency however with modern cyanine dyes. Certain ultraviolet absorbers useful for photographic filters, separate or coated with the silver layers, such as aesculin and umbelliferone, are natural products[22].

Vitamin B_1 was described in 1942 by Genda[23] and others in Japan as a sensitivity increasing agent for photographic emulsions. Vitamin B_2 (Riboflavin) was found by the author to be an effective catalyst in silver dye bleach solutions[24]. Vitamin C was patented as a developer, and as an ingredient in emulsions, by Vittum[25], and later as an anti-oxidant for photographic developers[26]. Among the hormones we find insulin mentioned as a retarding agent by Ruskin[27] and adrenalin described as a developer[28] by Rzymkowsky.

The biochemists find a number of their amines or amino acids represented in the emulsion maker's list of photographic chemicals. Creatine, arginine, and glycocyamine (guanidoacetic acid) were found by Elevegard[29] to be sensitizers in cellulosic silver halide dispersions and only recently spermin was patented by Lowe and Allen[30] as a speed increasing agent in gelatin emulsions. Photographic effects of thiosinamine, ergothioneine from blood[31], and other betaines found use in photography. Urea is an "old timer" in the photographic literature. Guanidocystine, in combination with aromatic sulfinic acids, was patented as a stabilizer by Mueller[31]. In the case of amines, it appears that their ability to form complexes with silver salts possessing various degrees of stability towards reduction, thus influencing the formation of ripening silver, may serve as an explanation for some of the effects described. Cystine in fixing solutions increases image brilliancy[32].

There is also some "undesired" biochemistry in the photographic industry. Every manufacturer of photographic products that are so highly sensitive both to light and to chemicals has been plagued from time to time by the appearance of so-called "emulsion spots", etc., which are attributed to inadequate filtration of the air in the plant of the emulsions themselves or are traceable to contamination of other raw materials such as paper, cellulose, or gelatin. Fortunately, such defects are less frequently encountered in modern air-conditioned plants. Archey in 1931[33] showed that at least some of these spots may have a biological origin. One interesting case, in which emulsion spots contained "crystalline dust", could be traced indirectly to a biological source—a mold contaminating the gelatin emulsion had produced oxalic acid which had reacted to form calcium oxalate in the gel.

This brief enumeration of the photographic use of some biochemical substances is far from complete, but the cited examples may illustrate sufficiently the fact that study of the mode of action of natural products in photographic preparations has produced significant and valuable results. Of particular recent interest are organic compounds capable of forming redox systems. Only recently W. G. Lowe[34] has theorized that the formation of the latent image, at least in the first stage, may be governed by a redox mechanism. This postulation appears to be based on the experimentally explored differential resistance of the sensitivity specks towards oxidizing agents. It is plausible then that certain organic redox systems, e.g. the disulfide-sulfhydryl system, may exert an influence on the speed and stability of photographic silver halide emulsions.

In retrospect it appears that the use in photographic emulsions of nature's products having complex structure did not only increase our knowledge of the photographic process itself but also contributed commercially to the practical improvement of modern photographic materials.

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A DRY BATTERY OPERATED ELECTRONIC FLASH UNIT

The authors wish to express their thanks to the firms that supplied special components and to acknowledge the valuable suggestions of a number of individuals. The low leakage electrolytic capacitors which made this work possible were supplied by Sprague Electric Company of North Adams, Massachusetts. Special low voltage flash tubes were furnished by General Electric Company, Nela Park, Cleveland, Ohio. Through the kind permission of Dr. Harold Edgerton of Edgerton Germeshausen and Grier, Cambridge, Massachusetts, we have been enabled to use the time-light curve for the experimental unit. Frank E. Carlson, E. B. Noel and L. Benjamin of General Electric Company at Nela Park, Cleveland, Ohio, made valuable contributions to this project, as did Sidney L. Chertok of Sprague Electric Company, North Adams, Massachusetts. W. H. Fritz of National Carbon Company, New York, contributed exposure data, information pertaining to the Medalist lamp head, and also made many helpful suggestions, including the original idea for the voltage doubler circuit.

P. A. MARSAL AND N. M. POTTER

A DRY BATTERY OPERATED ELECTRONIC FLASH UNIT

P. A. MARSAL AND N. M. POTTER*

ABSTRACT

The economical dry battery operation of Electronic Flashtubes as photographic illuminants is made possible by recent developments in electrolytic capacitors and lower voltage Flashtubes. Two portable units are described, one operating directly from a 450 volt battery, the other from a 225 volt battery by means of a high efficiency voltage doubler. The fact that no transformer is used in this doubler contributes to the high conversion efficiency and low idling power requirement. A detailed description of the operation of these units is given, including design equations, performance, battery life, etc.

ELECTRONIC FLASHTUBES, variously known as repeating flash lamps, etc., and sold under trade-marks such as "Speedlites", "Strobelites", etc., have been articles of commerce for over a decade. The earliest of these tubes operated in the range of 2000 to 4000 volts. Lower voltage tubes, such as the FT-110,[1] operating at 900-1000 volts, were later developed making it convenient to build portable equipment with electrolytic capacitors as the energy storage medium. However, electrolytic capacitors are not available for operation at much over 500 volts and in order to power the FT-110 lamp, such condensers must be connected in series.

With the series connection it is common practice to use a voltage divider across the power supply; appropriate taps being connected to the several electrolytic condensers in order that the rated voltage of each be not exceeded. This voltage divider, of course, consumes power, militating against the arrangement when the power source is a relatively small battery.

High voltage, high capacity electrolytic condensers have also been characterized by high leakage current. Small "B" batteries would therefore be discharged wastefully if connected across such condensers.

Recently, greatly improved capacitors have become available and these, along with still lower voltage lamps make possible the design of truly portable electronic photoflash equipment utilizing standard small radio "B" batteries as the power source.

Electronic Flash Equipment Design

Before discussing operating characteristics of electronic flash equipment, it is necessary to consider some of the features from the photographer's viewpoint. The requirements of a photographer can be stated in terms of light output, recharging time, size, and weight.

Within limits, the light output of a gas filled flash tube is proportional to the amount of electrical energy discharged through the tube.[2] It is customary to consider the electrical energy as the number of watt-seconds stored in a capacitor. This is given by Equation (1) in terms of capacitance and voltage.

$$W = \tfrac{1}{2} CE^2 \qquad (1)$$

where W = Energy in watt-seconds (joules).
C = Capacitance in farads.
E = Voltage.

The new low leakage capacitors, which were used in this investigation, were rated at 550 mfd., 450 volts. From Equation (1), this capacitor will store 55 watt-seconds of energy when charged to rated voltage. Experience of the authors has shown that a 50 watt-second power supply with a suitable flash tube will produce well exposed Super XX negatives using a Guide Number of 85 and normal development in D-76. Light output of this order of magnitude is sufficient to meet the needs of many amateur photographers. For others, requiring higher light levels, two of these capacitors can be used in parallel to give a 100 watt-second supply. This increases the Guide Number to 120 for the same negative material and development.

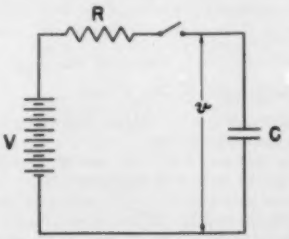


Fig. 1. Elementary charging circuit, showing capacitance and resistance in series.

The time required to charge a capacitor to a given voltage from a D.C. source depends on the resistance in the circuit (including the internal resistance of the source), voltage of the source and the capacitance. In the circuit shown in Figure 1, the capacitor voltage v, at any time after the switch is closed, is given by Equation (2).

* National Carbon Research Laboratories, Cleveland 1, Ohio.
Presented at the PSA National Convention in Detroit, Michigan 13 October, 1951. Received 10 September, 1951.

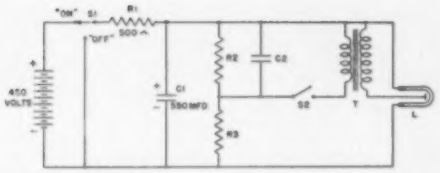


Fig. 2. Electronic flash circuit for 50 watt-seconds energy storage at 450 volts.

$$v = V\,(1 - e^{-t/RC}) \qquad (2)$$

where V = Source voltage.
R = Resistance in ohms.
C = Capacitance in farads.
v = Capacitor voltage.
e = 2.718 (base of Naperian logarithm system).
t = Time in seconds from instant of switch closure.

The charging time of such a circuit is usually referred to in terms of its "Time Constant". This represents the interval of time required for the capacitor voltage to reach $(1 - 1/e)$ or 63.2 per cent of its final value. The "Time Constant" of a capacitance in series with a resistance is given by Equation (3).

$$T_c = CR \qquad (3)$$

where T_c = Time constant in seconds.
C = Capacitance in farads.
R = Resistance in ohms.

When the time constant of such a circuit is known, the capacitor voltage will reach 95 per cent of its final value in an interval which is three times as long as the time constant or $3T_c$.

Simple Electronic Flash Circuit

With the new components a very simple circuit is possible. Such a circuit is shown in Figure 2.

When switch S_1 is turned "On" the energy storage capacitor C_1 charges to 450 volts and the trigger capacitor C_2 charges to a voltage determined by the values of the voltage divider resistors R_2 and R_3. When S_2 is closed C_2 discharges through the primary of the trigger transformer T and the high voltage developed in the secondary of the transformer ionizes the gas in the flash tube L and the energy stored in C_1 then discharges through the flash tube.

In this circuit the 500 ohm resistor R_1 serves two purposes. Its primary function is to permit the flash tube to de-ionize completely at the end of a flash. If there were no resistance in series with the battery the flash tube would continue to conduct and prevent C_1 from recharging. Its second purpose is to discharge capacitor C_1, as a safety precaution, when switch S_1 is turned "Off".

The energy storage capacitor C_1 must be of a special type having very low leakage current in order to realize satisfactory life and operating economy from a portable high voltage dry battery. For the same reason the voltage divider consisting of R_2 and R_3 in series should have a total resistance of five to ten megohms. The capacity of C_2 and the voltage to which it should be charged are determined by the characteristics of the trigger transformer T. For example, a General Electric Type 86G41 transformer requires a capacity of 0.25 mfd. charged to 160 volts. The trigger circuit switch may be either a manually operated push button type for "open flash" or "X" type shutter contacts for "synchro flash". When contacts built into the shutter are used to close the circuit to the trigger coil it is essential that a well designed coil be used, with reasonable energy input, so as not to damage the relatively delicate contacts.

Performance of Simple Electronic Flash Unit

The circuit of Figure 2 has a nominal rating of 50 watt-seconds. This is based on an unused battery of 450 volts giving a stored energy of 55 watt-seconds, from Equation (1), which drops to 45 watt-seconds when the battery voltage has fallen to 400 volts through use. If exposures

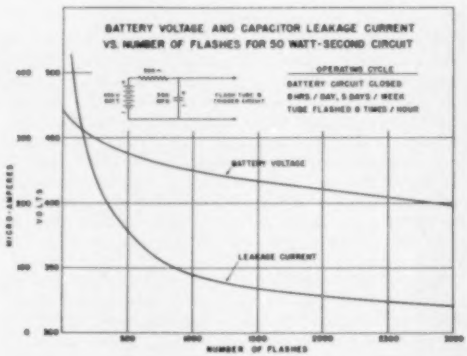


Fig. 3. Service test on "Eveready" No. 490 batteries operating 50 watt-second, 450 volt flash unit.

are based on the 50 watt-second nominal light output, and the battery replaced when it reaches 400 volts, the exposures would vary by only plus or minus 10 per cent throughout the life of the battery.

Service tests have been carried out using the circuit of Figure 2 and a battery consisting of five "Eveready" No. 490, 90 volt, "Mini-Max"* batteries connected in series. The battery circuit was closed for eight hours per day, five days per week, and the flash tube fired at regular intervals eight times an hour, giving a total of 64 flashes per day. Under these conditions 2900 flashes were obtained to the 400 volt end-point. The battery internal resistance was found to be 400 ohms initially, increasing to 550 ohms at the completion of the test. Closed circuit battery voltages and capacitor leakage currents for this test are shown in Figure 3.

The time constant of the circuit was measured at intervals throughout the battery service test. From these data the time required to recharge the capacitor to 95 per cent

* The terms "Eveready" and "Mini-Max" are registered trademarks of Union Carbide and Carbon Corporation.

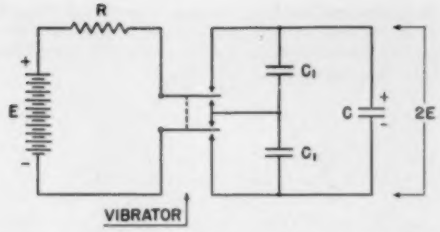


Fig. 4. Voltage doubler circuit using a split reed synchronous vibrator.

of its final voltage was found to be 1.9 seconds at the start of the test, increasing to 2.6 seconds at the 400 volt end point. This recharging time is exceptionally short compared to electronic flash equipment using a storage battery and vibrator.

Voltage Multiplying Methods

Numerous methods for producing high voltages from low voltage batteries have been proposed.[3] Low conversion efficiency has been the main objection to most of these systems. The circuit which has been applied most successfully to portable electronic flash devices uses a synchronous vibrator and voltage step up transformer, powered by a storage battery. Several difficulties arise when an attempt is made to replace the storage battery with a dry battery in such a circuit. The low conversion efficiency results in short battery life and high operating costs, or requires a large and bulky battery. The variable nature of the voltage of a dry battery presents a serious problem with respect to light output and exposure, which vary as the square of the voltage of the energy storage capacitor.

The use of a transformer in a voltage multiplying circuit has the further disadvantage that a relatively heavy current is drawn from a low voltage battery in the "stand-by" condition. This current is the sum of two components:

1. Leakage current in the secondary that is reflected back to the primary as a much higher value. This primary component of stand-by current is equal to the secondary current multiplied by the transformer turns ratio.
2. Transformer magnetizing current.

The resulting stand-by current drawn from a four volt battery can easily amount to 1 or 2 amperes in existing equipment.

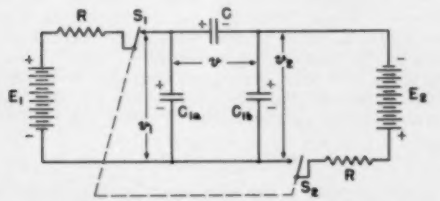


Fig. 5. Equivalent voltage doubler circuit. The capacitor polarities are shown for the first half cycle while S_1 is closed. The current through C is unidirectional.

Transformerless Voltage Doubling Circuit

A transformerless voltage doubling circuit has been developed and tested which has practically a 100 per cent conversion efficiency, exclusive of the power required to drive the vibrator. The basic circuit is shown in Figure 4. In this circuit R represents the internal resistance of the battery, C is a low leakage electrolytic energy storage capacitor connected in parallel with two "doubler" capacitors C_1. A split reed synchronous vibrator alternately charges the two capacitors C_1 to voltages which are very nearly equal to the battery voltage E. After a time interval, dependent on the circuit constants, the energy storage capacitor C becomes charged to almost 2E.

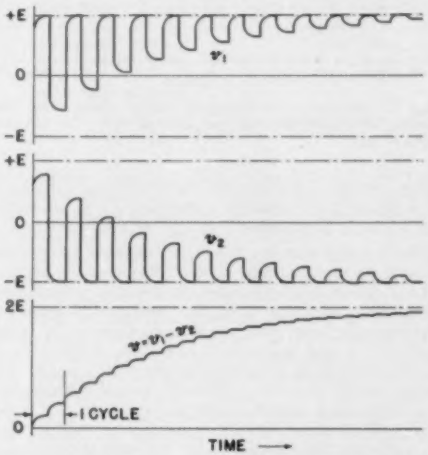


Fig. 6. Double circuit voltage wave forms. The wave shapes are determined by the time constant of the circuit.

The voltages appearing across the three capacitors, during a charging cycle, can best be explained by referring to Figure 5, which is an equivalent circuit for Figure 4 when switches S_1 and S_2 close alternately. In this circuit E_1 and E_2 are identical batteries, each having the same voltage as E in Figure 4.

The capacitor polarities in Figure 5 are shown for the first half cycle while S_1 is closed. When the capacity of C is much greater than that of C_1, the charge on C at the end of the first half cycle is determined by the charging current of C_{1b} which is in series with C across the battery E_1. During the second half cycle, when S_1 is open and S_2 closed, C receives a second increment of charge from the current through C_{1a} which is now in series with C across potential source E_2, and the polarities of C_{1a} and C_{1b} become reversed. It should be noted that the current through C is unidirectional. At any instant the voltage v is equal to the algebraic difference between voltages v_1 and v_2. The nature of these voltages is shown in Figure 6 where the rate of change with respect to time has been greatly exaggerated for the purpose of illustration.

The wave shapes of v_1 and v_2 are determined by the time constant of the circuit. This is equal to the internal

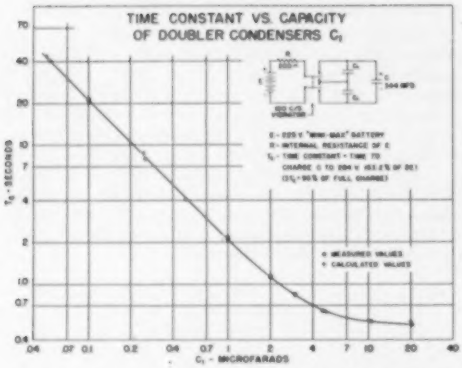


Fig. 7. Time constant of voltage doubler circuit. The "time constant" is almost inversely proportional to C_1 for values of 1 mfd or less.

battery resistance R times the total effective capacity of the series-parallel connected capacitors. As R approaches zero the wave shape approaches that of a square wave.

The charging time for this circuit depends on the capacities of C and C_1, the vibrator frequency f, the time interval during which the vibrator contacts are closed and the internal resistance R of the battery. Charging time measurements have been made over a range of values for C, C_1, R and f. Figure 7 is typical of the effect on charging time of varying the capacity of C_1. A 344 mfd. energy storage capacitor, 100 cycle/second vibrator with an 8 millisecond contact closure per cycle and a 225 volt battery of 200 ohms internal resistance were used for these measurements. The charging time is shown as the effective "Time Constant" of the complete circuit, i.e. the time in seconds to charge C to 63.2 per cent of 450 volts. It will be noted that the "time constant" is almost inversely proportional to C_1 for values of 1 mfd or less. Larger values of C_1 reduce the "time constant" at a decreasing rate until it finally approaches a limit which is a function of R and C.

From the experimental data and circuit analysis a semi-empirical Equation (4) has been developed for the effective circuit "time constant".

$$T_c = \frac{0.632C}{fC_1} + 8RCe^{-\,t/8RC_1} \qquad (4)$$

where T_c = Circuit Time Constant.
C, C_1 = Capacities in Farads.
f = Vibrator Frequency in Cycles/Second.
R = Internal Resistance of Battery in Ohms.
e = 2.718 (base of Naperian logarithm system).
t = Vibrator Contact "Closed" Time per Cycle in Seconds.

Inspection of Equation (4) shows that as the value of C_1 is reduced the last term approaches zero and the "time constant" is given by $\left(\frac{0.632C}{fC_1}\right)$ which represents the straight part of the curve of Figure 7. As C_1 is increased in value the charging time approaches a minimum which is a function of R and C. This can be demonstrated by substituting infinity for C_1 in Equation (4) which reduces it to $T_c = 8RC$. This represents the maximum rate at which energy can be transferred to C from the battery through its internal resistance. A suitable 225 volt battery for this application, consisting of two "Eveready" No. 490 batteries and one "Eveready" No. 455 battery in series, would have an initial internal resistance of 200-250 ohms increasing to approximately double these values when discharged to 190 volts. Very good agreement is shown in Figure 7 between the experimental data and the "time constant" values calculated from Equation (4).

Fig. 8. Working model 100 watt-second power supply incorporating the voltage doubling system described here. The total weight is 6½ lbs.

Fig. 9. Electronic flash head for Medalist II camera built to operate with the power supply shown in Figure 8.

Working Models

Figure 8 shows a 100 watt-second working model incorporating the voltage doubling system described in this report. The enclosure is a leather case measuring 4" x 4¾" x 7½". Total weight of the power unit is 6½ lbs.

Fig. 10. Electronic flash head using a Jen synchronizer ring for use with Leica cameras. A relaxation oscillator has been built into the head with its small neon tube visible through the plastic housing.

Two lamp heads were built to operate from this power supply; one, shown in Figure 9, for use with the Medalist II camera, the other, shown in Figure 10, to fit on the Leica. The Medalist II head is triggered by means of the "X" contacts built into the shutter. In the case of the Leica, a Jen synchronizer ring is used to actuate a small switch built into the lamp head. The switch is automatically positioned when the lamp is slipped into the accessory clip on top of the camera.

A relaxation oscillator has been built into the head. The small neon tube which forms a part of the oscillator is easily visible through the plastic housing. When the main storage capacitor is charged to 375 volts the neon tube starts to glow intermittently, thus indicating that the device is ready to fire. The neon tube flashing rate increases as the capacitor voltage builds up—thus providing a rough measure of battery condition.

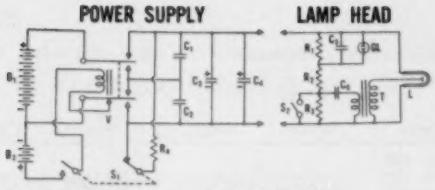
A wiring diagram for the working model is shown in Figure 11.

Performance of Model

It is customary to consider the duration of the flash as the time during which the light output is above one-third of the peak value. Figure 12 shows the light-time curve for the 100 watt-second model. From this it is apparent that the effective exposure time is close to one millisecond. Test exposures were made using both the Medalist II and Leica cameras. On the basis of these test exposures the following guide numbers are suggested:

	50 Watt-Sec. Unit	100 Watt-Sec. Unit
Plus X	60	85
Super XX	85	120
Daylight Kodachrome	25	35

The guide numbers suggested for black and white film are based on normal development in D76.



R_1 - 1.5 megohms
R_2 - 3.25 megohms
R_3 - 3.25 megohms
R_4 - 500 ohms, 5 watts
S_1 - On-off Switch
S_2 - Trigger Switch
B_1 - 225 v. Battery (2 "Eveready" No. 490 and 1 "Eveready" No. 455)
B_2 - 4.5 v. Battery (3 "Eveready" No. 1016-E)
C_1, C_2 - 1 mfd., 400 v.
C_3, C_4 - 525 mfd., 450 v. Sprague Electric Co., No. 2201, 2202 or FF-1
C_5 - 0.05 mfd., 200 v.
C_6 - 0.25 mfd., 400 v.
V - Oak V6815 Vibrator
L - G.E. FT-105 Flash Lamp
GL - G.E. NE-2 Neon Lamp
T - G.E. No. 86G41 Transformer

Fig. 11. Wiring diagram of 100 watt-second electronic flash unit using voltage doubler.

Laboratory tests have shown that the light output of this unit will drop by only one-half lens diaphragm stop after 750 flashes in the case of the 225 volt battery. A small 4½ volt battery was used in this unit to drive the vibrator. This battery consisted of three number 1016-E hearing aid "A" batteries. Initial current drain is 90 milliamperes and the vibrator will operate down to 3 volts. It is estimated that a service life of 22 hours will be obtained under these conditions. The measured time constant of this circuit is 6.5 seconds with new batteries. This is in good agreement with the 6.7 seconds calculated from Equation (4).

It is suggested that a more acceptable commercial design of this model would incorporate 3 "D" size flashlight cells. Three "Eveready" No. 950 (size "D") flashlight cells have more than enough energy to outlast the recommended 225 volt "B" battery, when used to drive the vibrator listed.

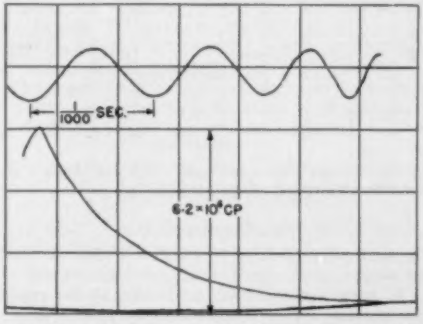


Fig. 12. Light output vs. time oscillogram for modified FT-110 flashtube at 100 watt-seconds at 450 volts.

By definition the time factor expresses a voltage, 63 per cent of final charge, which represents too great a departure from the nominal 100 watt-second rating. Therefore, the circuit values shown in Figure 11 were adjusted so that

Table I

CALCULATED PERFORMANCE OF FOUR DIFFERENT DRY BATTERY OPERATED FLASH UNIT POWER SUPPLIES

Types	Voltage	Weight	List Price	Circuit	Storage Capacitance	Stored Energy	Number of Flashes **	Cost Per* Flash
2-No. 490								
1-No. 455	225	2-½ lb.	$ 8.45	Doubler	525 mfd.	53 w.s.	1500	0.56 cents
2-No. 490								
1-No. 455	225	2-½ lb.	8.45	Doubler	1050 mfd.	106 w.s.	750	1.1 cents
5-No. 490	450	5 lb.	16.25	Direct	525 mfd.	53 w.s.	3000	0.54 cents
5-No. 490	450	5 lb.	16.25	Direct	1050 mfd.	106 w.s.	1500	1.1 cents

* Does not include vibrator driving battery, where required.
** To that voltage where light is reduced by ½ aperture stop.

the neon indicator starts to flash when the main storage capacitor is charged to 375 volts. The unit may be fired at this point with an output one-half lens diaphragm stop below the nominal 100 watt-second rating. The charging time to 375 volts was measured as 11.6 seconds with new batteries.

The results of service tests on the 225 volt battery used in this unit are shown in Figure 13. It is indicated that the charging time after 770 flashes reaches 30 seconds. If shorter charging times are desired they can be obtained by the use of higher vibrator frequencies or larger doubler condensers. For example, by using 2 mfd. doubler condensers instead of the 1 mfd. specified, the charging time is cut approximately in half, giving a range of 6 to 15 seconds over the life of the batteries.

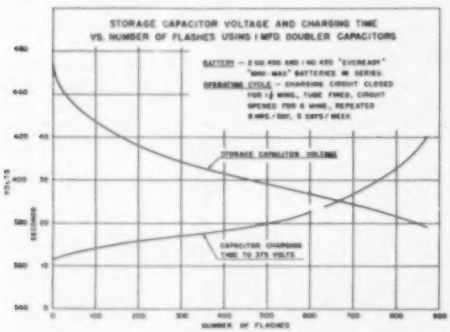

STORAGE CAPACITOR VOLTAGE AND CHARGING TIME
VS. NUMBER OF FLASHES USING 1 MFD. DOUBLER CAPACITORS
BATTERY — 2 NO. 490 AND 1 NO. 455 "EVEREADY" "MINI-MAX" BATTERIES IN SERIES.
OPERATING CYCLE — CHARGING CIRCUIT CLOSED FOR ½ MIN., TUBE FIRED, CIRCUIT OPENED FOR 6 MIN., REPEATED 8 HRS./DAY, 5 DAYS/WEEK
STORAGE CAPACITOR VOLTAGE
CAPACITOR CHARGING TIME TO 375 VOLTS
VOLTS
SECONDS
NUMBER OF FLASHES

Fig. 13. Service test on 225 volt "Mini-Max" battery operating a 100 watt-second voltage doubler flash unit.

Synchronization

The electronic flash lamp fires instantly when the switch to the trigger coil is closed, making it ideal for use with the "X" type contacts built into many of the modern camera shutters. With shutters not equipped with flash contacts, it is necessary to delay the firing of the lamp until the shutter blades are fully open, a matter of 3 to 5, milliseconds after tripping for typical shutters.

In many cases a solenoid is used to trip the shutter and in these cases the delay after energizing the solenoid until the blades are fully open amounts to 20 milliseconds.

There are various methods[4,5] for effecting the delay necessary to synchronize the light flash with the shutter open interval but these are beyond the scope of this paper.

The Leica camera presents a special case. The focal plane shutter curtains are fully open momentarily at speeds of 1/30 second and longer and it is during this open interval that the light is flashed. This is accomplished by means of a switch located in the lamp head in such a position as to engage a cam attached to the shutter setting dial. With proper adjustment the switch closes just as the leading curtain finishes traversing the film aperture and before the lagging curtain starts to move.

Operating Cost

The experimental work indicates that the battery cell size incorporated in the "Eveready" No. 490 90 volt "B" battery is the best compromise between operating economy and portability. The same cell size is used in the "Eveready" No. 455 45 volt battery. These batteries are widely used as the "B" supply in a variety of popular small portable radio receivers.

Two basic power supply designs are suggested in this report. First, a simple unit similar to that of Figure 2, using a 450 volt battery and a capacitance value adequate for the photographic requirement. Second, a voltage doubling unit similar to that of Figure 11; again using an adequate capacitance value. The same flashing head may be used with either design.

Table 1 has been prepared to show what might be expected of four different power supplies, all designed to charge an adequate capacitance value to a nominal maximum of 450 volts. The values in the table are necessarily approximate, but are sufficiently accurate for a valid comparison.

It is apparent that the operating cost, using the suggested battery types, is roughly independent of the battery arrangement and proportional to the stored energy (or required light output).

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The Determination of Silver in Photographic Images Using I^{131}, Radioactive Iodide*

A. E. Ballard, G. W. W. Stevens, and C. W. Zuehlke

SUMMARY

Two methods utilizing radioactive I^{131} are compared with the potentiometric method for determining the silver in developed photographic images. Both are based on the quantitative conversion of the silver image to silver iodide using an appropriate ratio of active to natural iodide. Both of these methods give an accuracy of approximately 1.5% and a precision of ± 1.1%, when 2000 counts are recorded for each specimen. Either method is adaptable to the routine determination of silver in a large number of samples.

PHOTOGRAPHIC materials are mostly designed to indicate "exposures" by means of a variation in blackening, the measurement of which constitutes the chief method for assessing their performance. Valuable additional information can also be obtained by analytical determinations of the mass of developed silver per unit area in photographic images. Thus, in the photographic industry, the concept of the photometric equivalent**, i.e., the ratio of the mass of silver to the optical density, has proved very useful. Certain scientific applications of photographic materials also require determination of the mass of developed silver.

A variety of analytical methods have been used in the past to measure the mass of developed silver in the steps of a sensitometric strip. Sheppard and Ballard[1], for example, have shown that this determination could be made with an accuracy adequate for most purposes by using a colorimetric method based on the formation of silver sulfide. In more recent years, volumetric methods using potassium iodide with a potentiometric or amperometric end-point have been preferred. In either, a known area of film is punched out from the image of each step of a sensitometric strip. The silver is removed separately from each punched-out area by treatment with nitric acid and the titration is carried out in the presence of an acetate buffer.

These methods, when applied to samples having an area of approximately one square centimeter, and when using $N/10{,}000$ iodide solution, provide results having an accuracy of approximately ± 2%. As the amount of silver available for analysis decreases, the accuracy of the determination likewise decreases. At an optical density of 0.1, for example, where approximately only 0.01 mg of silver may be titrated, the accuracy of the method approximates ± 5%. Since the precision of the density measurement is similarly related to the mass of silver in the sample, the volumetric methods reasonably have been considered adequate for the determination of photometric equivalent. Greater sensitivity could, with loss of convenience, be achieved by taking larger areas of film. Such techniques are, however, relatively tedious and difficult, in which connection Mees[2] has stated:

"It would be more logical if the effect of exposure were measured in terms of the quantity of metallic silver produced; and it is unfortunate that the measurement of the silver in the image is so difficult, since it is probable that the variation in the covering power of the silver plays a much larger part in photographic effects than is generally realized."

Analytical procedures based on the use of radioactive isotopes may be usefully employed in this connection. Baenziger[3] has proposed the use of radioactive cobalt for determining the silver in X-ray images, by converting the image to cobalt ferrocyanide using $cobalt^{60}$. The radioactivity of the sample measured with a Geiger counter serves as a direct measure of the integrated intensity of the X-rays producing the image.

The present paper describes similar experiments carried out with radioactive $iodine^{131}$. The methods used are shown to give an accuracy of ± 1.5%, and to be applicable to the determination of smaller quantities of silver than could previously be conveniently detected. They can also be directly applied to the determination of silver bromide and chloride, probably also to silver sulfide.

Method for the Assay of Silver by Radioactive Tracers

The assay of a silver image by radioactive tracers involves the following steps:

1. Chemical conversion (or "toning") of the silver image resulting in the quantitative deposition of an insoluble compound containing the radioactive tracer.

2. Washing to remove all the tracer which has not reacted with the image.

3. Determination of the activity of the specimen with a Geiger-Müller counter, accompanied by comparison with the activity of a sample of known silver content submitted to the same processing procedures.

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** Photometric equivalent (P) $= \dfrac{\text{grams Ag/100 cm}^2}{\text{density}} = \dfrac{1}{\text{covering power}}$

Pretreatment

The sample must be properly fixed and washed prior to the application of these methods. The presence of silver bromide or silver chloride or soluble silver will cause the deposition of additional I^{131} and lead to high results for metallic silver. The presence of hypo or other silver halide solvents may lead to low results.

The gelatin layer should also be brought into a condition permitting the complete removal of unreacted tracer from the layer, by insuring that it is adequately hardened. If tests indicate that layers containing no silver retain an unduly high activity after washing, they should be treated for 5 minutes in a formalin hardener and rinsed for 10 minutes before drying prior to the conversion of the image.

Conversion to a Radioactive Form

A wide variety of chemical conversions have been used to modify the color or increase the density of developed silver deposits. Most of these could be used for the image-wise precipitation of a radioactive ion. The selection of an appropriate ion is dictated by the following considerations:

1. The radioactive isotope should have neither too long nor too short a half-life. A long half-life complicates the disposal of residues, while too short a half-life necessitates corrections for the decay occurring during a single determination.
2. The silver image should be completely and quantitatively converted by a simple operation.
3. The precipitated compound should be very insoluble both in the treating and in the washing solutions, particularly when dealing with images of low silver content where the loss of even minute amounts may represent a large fraction of the total.
4. Chemical or physical combination with the gelatin or other vehicle should be small. If such combination does occur, its removal without affecting the product precipitated by reaction with the image should be a simple operation. This consideration is also especially important for images of low silver content.
5. The isotope should preferably be available with high specific activity, so that the method will give the highest possible sensitivity when needed.

Iodide ion, to a very satisfactory extent, fulfills all these requirements. A radioactive isotope, I^{131}, emitting both β particles and gamma rays[4] is available from the U. S. Atomic Energy Commission and the Atomic Energy Research Establishment, Harwell. It is supplied as a weakly basic solution of sodium iodide containing up to 5 millicuries of activity per milliliter.

Iodination of Developed Images

The most direct method of iodination, namely, by bleaching the developed image with a solution of free iodine, is undesirable because of the health hazard arising from the volatility of iodine as well as its known reaction with gelatin. Two alternative methods have therefore been examined in the present communication.

In the first, the silver image is bleached to silver bromide, and is then converted to silver iodide. It is well known that silver images can be bleached to silver bromide by use of a ferricyanide-bromide bleach (as used for toning prints) and that the reaction is essentially complete. The silver bromide deposit can then be completely converted to silver iodide by reacting with a solution of soluble iodide.

The second method combines the two operations of bleaching a silver image and converting it to silver iodide in the same solution. Potassium ferricyanide readily bleaches a silver image to silver iodide in the presence of soluble iodides and this solution does not contain free iodine at a pH of 7.0 or above.

The original sample of radioactive isotope is diluted with a suitable amount of inert carrier with either method, and this allows the final activity of the specimens to be varied at will within very wide limits. It is suggested that preliminary tests should be made to determine a dilution ratio resulting in from 2000-4000 counts per minute for the units of the image most rich in silver. This is the highest counting rate which does not require an appreciable correction for the resolving time of many counters. Increasing the ratio of stock solution of high activity to another solution of natural iodide can be used to compensate for the decay of the isotope, or for the treatment of images of low silver content.

The volumes of radioactive solution used are dictated by the requirements of the individual worker. For routine work this is fixed only by convenience, but the volume may have to be kept to a minimum when working with samples very poor in silver, or when work is carried out sporadically on a small scale. When ample solution is available, it can be applied in deep battery jars or in glass trays. Less solution is required if the emulsion is supported face downwards 2 millimeters above the bottom of the tray, and the solution is allowed to run to and fro under the emulsion as the tray is rocked. An even greater economy can be effected by applying the solution with a pipette to the dry emulsion surface; the method used with the experiments on single-layer plates described below under "Experimental".

The conversion reaction must be continued until the reaction, as indicated by preliminary control tests, is compiete. It is, of course, essential to insure that the solution still contains an appreciable concentration of iodide ions after completion of the reaction. High concentrations of soluble iodide can, however, dissolve silver iodide from gelatin layers and concentrations of iodide above 1% should not therefore be used.

Washing

The specimens must be thoroughly washed after treatment with the radioactive solution, so that fixed but undeveloped controls show constant low radioactivity which should, in most cases, not give a significant increase in counting rate over the background. This can be readily done with coatings on films or plates but paper bases might be expected to retain considerable radioactivity after prolonged washing.

Counting

The method of counting or assaying the radioactive images is similar to that used in other applications of radioactive tracers. A known area of each unit of the image is presented in turn at a fixed distance from and position relative to a Geiger-Müller tube. The instrument

is then used to record the counting rate showing either the number of counts obtained in a given time, or the time taken to record a predetermined number of counts.

With images on film, a small area of the treated film can be punched from each step. Sheppard and Ballard[1] showed that areas of about 0.5 sq. cm. can be punched out with a variability of less than 1%. The counting of such punched samples represents an ideal condition, since all possibility of radiation from adjacent areas influencing the counting rate is eliminated. Areas cannot, however, be punched from glass plates, nor is it convenient to cut known and reproducible areas from glass plates by other methods. It is readily possible, as an alternative, to cut an area from the plate slightly larger than that desired for measurement, and to define precisely the area counted by use of a metal mask having an appropriate aperture. The mask must clearly be substantially opaque to the radiation detected by the counter. Sheet brass 3 mm. thick effectively absorbs the β-particles from I^{131}, but largely transmits the gamma rays. β-particle counters are relatively insensitive to gamma rays, as such, but they do give some response to gamma radiation due to secondary electrons formed by gamma rays in the active volume of the counter. For this reason it is not possible to mask out perfectly an unwanted area of a photographic image.

The influence of gamma-ray penetration of the mask was in one case examined by measurements on a uniformly fogged film treated with radioactive iodine, from the center of which was punched a circle slightly larger than the aperture in the mask. The conditions of measurement are illustrated in Figure 1 and the results obtained are shown in the following table.

Table I

INFLUENCE OF GAMMA-RAY PENETRATION OF SHEET BRASS MASK UNDER CONDITIONS SHOWN IN FIGURE 1.

Condition of Measurement	Area Covered by Mask	Area Exposed through Mask	No. of Counts in 3 Minutes
A	0.05 sq. cm.	0.21	10,015
B	11.80 sq. cm.	0.21	12,868
C	11.75 sq. cm.	—	2,863

This table indicates a counting rate of 50,000/sq. cm. through the aperture and only 240/sq. cm. for the area covered by the mask. It shows that surrounding the aperture with an area of film 56 times that exposed through the aperture, increased the counting rate by only 28%. The error produced when the silver exposed through the aperture was surrounded by an equal amount of silver behind the mask thus would be very small.

The error due to gamma-ray penetration could thus be eliminated by comparing the counting rate when the specimen is covered (a) with the mask, and (b) with a piece of brass without an aperture. The difference between the readings then indicates only the β activity passing through the aperture.

Standardization

The use of radioactive tracers provides a particularly convenient method for comparing the relative amounts of silver in photographic deposits. If an absolute value for silver content is required, it is only necessary to compare the count rate of the unknown with that of a standard sample containing a known amount of silver carried through the same procedure by use of the same solutions. The standard sample should resemble the unknown with respect to grain size and gelatin thickness. By use of such a calibration, all of the experimental variables such as decay of activity, geometry, and efficiency of the counting system are effectively cancelled and may safely be ignored.

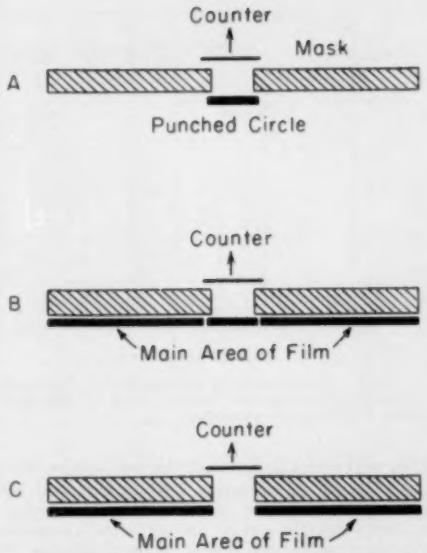

Fig. 1. Conditions used for counting samples after the silver image has been converted to silver iodide by means of radioactive sodium iodide.

Experimental

Preliminary tests were made to study the conversion of silver bromide to silver iodide by treatment with iodide solutions. Single-grain layers of a silver bromide emulsion were treated for varying periods of time with an excess of sodium iodide solution containing I^{131}. The activities of the coated samples reached essentially a maximum after 3 minutes, indicating that silver bromide grains of a size likely to be produced by the bleaching of a silver image are rapidly and completely converted to silver iodide.

Further preliminary work was done on single-grain-layer plates giving an optical density of less than 0.1 upon complete development. Test pieces one cm. square were converted to silver iodide using a solution containing 10 microcuries of I^{131} per mg. of natural iodide. These samples gave more than 2000 counts per minute, which rate could have been greatly increased by use of solutions of higher specific activity. This work indicates that the method can be designed to give a high order of sensitivity. Similar measurements were made on single-layer test pieces fixed under standardized conditions in hypo solutions of varying concentrations. The results, plotted in Figure 2, show that the fixation of even such dilute coatings may

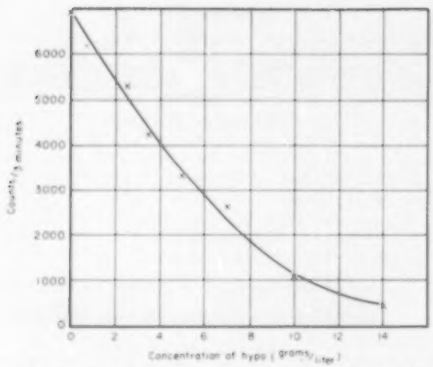

Fig. 2. Measurements of radioactivity of single-grain layers of silver bromide emulsion fixed in hypo solutions of varying concentrations.

be followed with ease by use of the radioactive method.

Two procedures employing I^{131} are suggested below. Experimental work was done to demonstrate that the measured radioactivity of the iodized image is proportional to its silver content over a wide range of densities. Three common types of film, i.e., fine-grained, medium-grained, and coarse-grained emulsions, were used. Sheets of the film ($8\frac{1}{2}$" x 10") were given a step-wedge exposure to provide 10 areas (approximately 1" x 8" each) of uniform density after development. The samples were double-fixed and washed thoroughly before use. Adjacent areas were taken for silver determination by the potentiometric-titration method and the radioactive-iodine methods.

Potentiometric Titration of Silver

Reagents:

Nitric acid
Ammonium hydroxide
Acetic acid, glacial
Potassium iodide solution, 0.0001 and 0.001 *N*, standard.
Silver nitrate solution, 0.0001 and 0.001 *N*, standard.

Procedure:

Punch out an 8 mm square area of film (for very low densities larger areas should be taken) and treat it with 1 ml of concentrated nitric acid. Warm gently until the emulsion layer has cleared and dissolved. Cool. Add 2.5 ml of concentrated ammonium hydroxide and 2 ml of glacial acetic acid. Dilute to 35 ml and titrate with standard potassium iodide, using a silver-calomel electrode pair to detect the end-point. Choose an appropriate concentration of potassium iodide solution to provide a convenient titrating volume. Standardize the potassium iodide solution by the same procedure against a standard silver nitrate solution of approximately the same strength.

The Radioactive Iodide Method

Reagents:

Buffer solution: 10 g sodium acetate dissolved in 100 ml water and glacial acetic acid added to pH 7.4.

Powdered potassium ferricyanide.

Bleach solution: 50 g of potassium ferricyanide and 10 g potassium bromide made up to one liter with water.

I^{131} solution "A": One millicurie I^{131} plus 2 mg natural potassium iodide diluted to 100 ml (one ml equivalent to 10 microcuries as prepared).

I^{131} solution "B": Transfer an amount of I^{131} solution "A" containing 10 microcuries of activity to a 100-ml volumetric flask. Add 5 ml of buffer solution and 0.22 g natural potassium iodide and dilute to volume. 100 ml of this solution is sufficient to process 100 cm² of developed film. After one half-life (8 days) has elapsed, a fresh solution should be prepared (or the old solution should be enriched) using an appropriate amount of solution "A". In this way it is easily possible to use a 1 millicurie supply of I^{131} over a period of 6 eight-day half-lives providing 100 silver determinations during each half-life period.

Procedure (Two-bath method)

Immerse the strip of developed film in the bleach solution for 30 minutes with intermittent agitation. Wash the sample for 15 minutes in running water and rinse with distilled water.

Transfer one ml of I^{131} solution "B" for each square centimeter of sample area to a glass tray. Tilt the tray so that the solution runs to one end, immerse the sample strip, and rock the tray intermittently in subdued light for 60 minutes. Remove the strip, using forceps, and rinse briefly in a tray containing 100 ml of water. Hang the strip for 20 minutes in a mechanically stirred bath containing approximately 5 liters of 0.5% sodium bicarbonate solution. Repeat the washing for a second 20-min. period in a fresh bicarbonate bath. Hang the strip to dry.

Procedure (One-bath method):

Transfer one ml of I^{131} solution "B" for each square centimeter of sample area to a glass tray. Add 0.05 gram of powdered potassium ferricyanide for each milliliter of solution and rock the tray until solution is complete. Immerse the strip of developed film and allow to stand one hour with occasional rocking. Remove the strip using forceps, rinse, wash, and dry as directed in the two-bath procedure described above.

Counting the Samples:

Punch a circle, 8 mm in diameter, from each density area and count the activity of each punch-out, allowing enough time to record approximately 2000 counts. Calculate the counts per minute corrected for background. Count a standard sample of known silver content of the same film type which has been treated in the same way with the same I^{131} solution "B". Calculate the silver content of the sample by use of the formula:

$$\underset{\text{(sample)}}{\text{Mg Ag/cm}^2} = \underset{\text{(standard)}}{\text{Mg Ag/cm}^2} \times \frac{\text{cts./min (sample)}}{\text{cts./min (standard)}}$$

Each sample should be placed in exactly the same position, directly below the window of a Geiger-Müller tube for counting. In our work, this was achieved by use of a plastic support for the Geiger-Müller tube, bearing a removable brass plate properly positioned below the tube. A circular depression, approximately one mm. deep ma-

Table II

MILLIGRAMS OF SILVER FOUND BY IODINATION TWO-BATH METHOD

Milligrams of Silver per Square Centimeter

Emulsion Type	Optical Density	Potentiometric Method	Two-Bath Iodination Radio-Method			Average % Error	Average % Deviation from Mean
Fine-Grained Positive	0.20	0.020	0.021	0.020	0.019	3.3	3.3
	.50	.054	.053	.054	.054	0.6	1.1
	.76	.079	.079	.080	.078	0.8	0.8
	.99	.102	.102	.102	.101	0.3	0.4
	1.28	.127	.130	.129	.126	1.6	1.2
	1.60	.153	.153	.153	.152	0.2	0.2
	2.00	.185	.188	.188	.188	1.6	0.0
	2.34	.210	.208	.209	.208	0.8	0.2
	2.64	.229	.234	.235	.231	1.9	0.7
	3.00	.252	.254	.256	.260	1.8	0.9
						1.29	0.88
Medium-Grained Emulsion	.04	0.006	0.004	0.005			
	.21	.059	.057	.054	0.060	4.6	3.5
	.52	.130	.131	.126	.131	1.5	1.7
	.78	.182	.187	.183	.184	1.4	0.8
	1.03	.232	.237	.236	.232	1.3	0.8
	1.34	.287	.289	.284	.284	0.9	0.9
	1.64	.332	.336	.337	.336	1.4	0.1
	2.03	.389	.392	.402	.392	1.6	1.1
	2.33	.421	.416	.428	.415	1.4	1.3
	2.60	.454	.443	.455	.454	0.9	1.1
	2.97	.486	.480	.499	.473	2.2	2.1
						1.72	1.34
Coarse-Grained Negative	Fog	0.054	0.049	0.054	0.053	0.049	5.2	4.4
	.25	.095	.091	.090	.095	.092	3.2	1.6
	.65	.260	.260	.261	.265	.260	0.6	0.7
	.92	.338	.334	.342	.333	.338	1.0	1.0
	1.14	.396	.405	.408	.392	.400	1.8	1.4
	1.43	.451	.456	.456	.467	.457	1.8	0.9
	2.14	.558	.567	.564	.560	.573	1.4	0.7
	2.43	.598	.597	.591	.595	.600	0.6	0.5
	2.74	.633	.632	.627	.628	.612	1.3	1.0
	3.09	.668	.662	.659	.668	.657	1.0	0.5
							1.79	1.27

chined in the center of the plate, was used to hold the sample and prevent its movement.

Statistically, it is necessary to record 2050 counts to obtain a result having a probable error of 1.5%. For the higher optical densities, an accuracy of this order is useful. At the lower optical densities where the density cannot be read with high precision, the requirements of the silver determination are (at least for measurements of photometric constant) proportionately less. At a density of 0.20, for example, the precision of the density reading is not better than 4% and 260 counts would yield a counting precision equivalent to that of the density reading.

Blank determinations were run on plain gelatin coatings, using both of the procedures outlined above. In either case, the amount of active iodide entering into combination with the gelatin was not detectable, using the usual counting times.

The results reported under "mgs silver found by iodination" in Tables II and III were calculated by dividing the counts per minute observed for each punch-out, by the ratio of $\frac{\text{average counts/min}}{\text{average Ag mgs/cm}^2}$, of all of the steps for that iodination series, instead of using the formula given above, which uses only one standard silver step and would be the one used in practice when a series of unknown silver content steps were to be determined. This was done to provide a clearer picture of the reproducibility of the iodination and counting procedures. The tables show that the procedures can be carried out on any of the three emulsions used with an over-all error not greater than 2%.

In the tables, the values given in the column headed "Average % Error" were calculated (disregarding sign), assuming that the values for silver by the potentiometric method are correct. Since this is not necessarily true, the values in this column are actually a measure of the *precision* of the two methods combined. They are also the best measure available for the *accuracy* to be anticipated for the radioiodination method as it will generally be applied in practice where we shall be concerned with the same sources of error, namely: (a) the error of the potentiometric method for silver in the standard sample, and (b) the error in the radioiodination steps of the analysis.

The values given in the column headed "Average % Deviation from Mean" were calculated using the results of the radioiodination method only. These values are an exact measure of the *precision* of the radioiodide method as it will be applied in practice. Any errors in standardization affect all of the results proportionately and, therefore, have no bearing on precision.

Table III

MILLIGRAMS OF SILVER FOUND BY IODINATION ONE-BATH METHOD

Milligrams of Silver per Square Centimeter

Emulsion Type	Optical Density	Potentiometric Method	One-Bath Radioiodination Method			Average % Error	Average % deviation from Mean
Fine-Grained Positive	0.03*	0.0015	0.0016	0.0015	0.0013		
	.20*	.020	.020	.021	.020	2.2	0.2
	.50*	.054	.054	.054	.055	0.5	1.2
	.76	.079	.076	.079	.078	1.6	1.4
	.99	.102	.103	.102	.099	1.3	1.6
	1.28	.127	.128	.129	.129	1.3	0.3
	1.60	.153	.152	.152	.153	0.5	0.3
	2.00	.185	.188	.183	.183	1.2	1.2
	2.34	.210	.208	.206	.209	1.1	0.5
	2.64	.229	.238	.232	.230	1.9	1.3
	3.00	.252	.255	.250	.262	1.9	1.6
						1.5	1.0
	* A higher concentration I^{131} bath was used						
Coarse-Grained Negative	Fog	0.054	0.051	0.051		5.6	0.0
	0.25	.095	.093	.091	0.094	2.4	1.2
	.65	.260	.254	.260	.256	1.3	0.9
	.92	.338	.341	.330	.332	1.7	1.3
	1.14	.396	.399	.410	.393	1.7	1.6
	1.43	.451	.453	.449	.452	0.4	0.3
	2.14	.558	.564	.564	.567	1.3	0.2
	2.43	.598	.594	.598	.603	0.5	0.5
	2.74	.633	.636	.634	.632	0.3	0.2
	3.09	.668	.669	.664	.669	0.3	0.3
						1.55	0.65

Discussion

The procedures just described were designed to accommodate a range of grain sizes including all the common types of film. Complete conversion to silver iodide is obtained even with relatively coarse-grained negative materials. For fine-grained emulsions, a 30-min iodination was found to be sufficient. Preliminary work with extremely coarse emulsions (rapid X-ray film) indicates that conversion is not entirely complete in 60 minutes, but that satisfactory results may be obtained by extending the time to 120 minutes.

The iodination method is readily adaptable to the routine determination of silver on a large scale, since a large number of samples can be processed simultaneously and need only be cut up just before counting. Moreover, automatic counting equipment is now available which will count 25 samples without attention and record the activity on a printed tape.

The greatest advantages of the iodination method over the potentiometric method will only be realized if a large number of analyses are required. In a few special cases, where extreme sensitivity is required, the radioiodination method offers an additional advantage. For example, when only a very small image is available, as in the case of X-ray crystallographic patterns, or when the optical density is very low, the radioiodination method would be preferred.

The method may be applied, not only to silver images, but to silver bromide or silver chloride coatings as well. Silver sulfide images may be converted to silver chloride by treatment with permanganate and hydrochloric acid, or converted to silver bromide by treatment with bromine water. The silver chloride or silver bromide may then be converted to silver iodide in the usual way.

References

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